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ON THE VELOCITY OF LIGHT IN A MAGNETIC FIELD.

By John Mills.

SEVERAL investigations have at various times been undertaken to determine the nature of the Faraday "effect." The kinematical explanation of the rotation of the plane of polarization in natural rotatory substances by the assumption of two oppositely polarized circular components which travel with different velocities has led many investigators to a similar explanation in the case of a magnetic rotation of the plane of polarization. The more important of these investigations of the velocity of light in traversing a medium in an electromagnetic field are those of Messrs. Righi,[1] Brace[2] and Morley and Miller.[3] In every case the method has been to note the shifting of the interference bands formed by the divided portions of the same beam, one portion of which has traversed a medium in a magnetic field.

The investigation which is here described was performed with the apparatus granted to Messrs. Morley and Miller by the A.A.A.S. Their apparatus consisted of the more general type of a Michelson interferometer in the path of each ray of which was placed a tube of carbon bisulphide, surrounded by a coil and supported independently of the coil. The coils were differentially wound and each winding

[1] Nuov. Cim., 3, 1878, Beibl. 2, p. 715.

[2] Wied. Ann., 26, p. 576, 1885.

[3] Phys. Rev., 7, p. 288, 1898. See also Becquerel, Compt. rend., 88, p. 334, 1879, Beibl. 4, p. 624. Cornu, Compt. rend., 99, p. 1045, 1884, Beibl. 9, p. 273.

had independent terminals allowing the separate windings to be connected in series or differentially. Connecting the windings of one coil in series and those of the other differentially they obtained the same current and consequently the same heating effect in both, while only one coil acted as a solenoid. By a proper adjustment of their apparatus fringes were visible formed not only from the end mirrors of the interferometer but also two other sets one from the two glass plates covering the nearer ends of the two brass tubes and another from the plates at the further ends. Any shifting due to mechanical causes was then observable in the last two sets. A slight displacement noticeable on the making or breaking of the current circuit — but not apparent in the last two sets of fringes mentioned above, and therefore due to change in the sulphide — many times however as large as the effect suspected from the mathematical analysis of Mr. Eddy,[1] suggested a change in the density of the carbon bisulphide. Experiment failed however to detect any such change of density or volume. Using natural light from a sodium burner or sometimes interposing a Nicol prism they were unable to observe any shifting of the fringes indicating a change in velocity.

In the present experiment two changes were made in the method. First: the light used was passed through a $1-4\,\lambda$ plate after leaving the Nicol, for both Righi and Brace had noted in their researches that no shifting occurred or was to be expected for plane polarized light. Second: the chance of a shifting of the bands due to any mechanical cause was entirely eliminated by the use, instead of a single quarter wave plates of a Bravais double plate giving one half of the field of right- and the other half of left-handed circularly polarized light. The interference bands were then adjusted perpendicularly to the dividing line of the plate. Any shifting then due to mechanical causes would be in the same direction for both sets of bands; on the other hand any displacement of one half over the other would indicate a differential change in velocity. The separate windings could now be connected in series, making both coils solenoids and disregarding the mechanical effect of their juxtaposition. By these two means for the same current as before an effect of four times the magnitude was to be expected.

[1] PHYS. REV., 7, p. 283, 1898.

With the apparatus just described a distinct shifting of the fringes was noticed, and this shifting increased with the current. By interposing a rheostat in the system the current could be gradually increased until the shifting amounted to a full band — that is until the fringes again coincided. Then using about this same intensity of current the connection was made and the current adjusted more delicately with the rheostat until the coincidence appeared perfect. The writer observed at the telescope. The ammeter readings, however, were taken by an assistant and were not announced until the set was completed. The total drop of potential across the terminals of the system was changed after every other reading by the addition or subtraction of a portion of the storage cells used. In this way the observer was ignorant of the probable current readings for various positions of the rheostat lever arm. As the light forming the fringes had traversed in each tube some 150 centimeters of the sulphide fringes formed could not be read accurately much beyond 1–15. For example: the largest deviation from the mean in the case of one band (see Table I.) was .93 ampere, giving a sensibility of about one part in fifteen.

A more recent paper of Mr. Brace[1] has shown that the velocity of a circular ray in the direction of the amperian currents is accel-

TABLE I.

For a displacement of one band.

Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.	Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.
13.4	367.1	13.5	369.8
13.6	372.6	13.2	361.7
14.15	387.6	13.3	364.4
13.6	372.6	13.5	369.8
14	383.5	12.5	342.5
13.25	363	13.4	367.1
13.2	361.7	13.45	368.5
13.6	372.6	13.45	368.5
13.5	369.8	13.7	375.3
12.9	353.4		
13.4	367.1		Mean 367.9°

[1] The Observation of the Resolution of Light into its Circular Components in the Faraday Effect, *Phil. Mag.*, April, 1901, p. 464.

erated. It was assumed then that the effect observed was due to that cause. To check the results obtained with the corresponding rotation which would have been noticed in the case of plane polarized light a set of readings of the current necessary to rotate the plane of polarization 90° was taken for each coil. For one coil this value was found to be 13.06 amperes, for the other 13.23. Of these sets the mean is 13.14 amperes. The accuracy of this result is within one per cent. The current then that would be necessary in the case of a series connection to produce a shift of one band would be 13.14. In the preceding table it is to be noted that the current mentioned above with the form of apparatus used is equivalent to a rotation of the plane of polarization of 180°, that is to a difference in phase between the two circular components of 360°.

TABLE II.

For a displacement of three bands.

Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.	Ammeter Readings.	Corresponding Difference of Phase of the Two Circular Components.
39	1067°	42	1150
38	1041	40.5	1110
41	1123	40	1093
39	1067	40.5	1110
39.5	1082	41	1123
40	1093	42	1150
41.5	1136	40.5	1110
40.5	1110	39	1067
40.5	1110	40	1093
39	1067		
40.5	1110		Mean 1101°

A further set of readings was taken for a larger current. The system was connected with the 500-volt power circuit of the local traction company. A water rheostat was used and both the rheostat and ammeter manipulated by an independent observer. The current was increased until the writer had counted three full bands; upon the coincidence of the third the ammeter reading was taken at his call. The current was then still further increased until the coincidence was no longer perfect and decreased at the observer's call until the coincidence of the third band again seemed perfect; at this

point another ammeter reading was taken. Owing to the rapidly changing current due to the heating effect on the coils and the rheostat the ammeter readings could not be taken more accurately than within two per cent. There was lacking as well the deliberation of setting possible for a smaller current, as the fringes formed were quickly susceptible to changes. A difference of one tenth of a band was easily observable, however. In general only one or two readings could be taken at a time. The coils were then allowed to cool before the next reading.

A shifting of four bands was noticed for a current of some 52 amperes, but the heating effects of such a large current made it impossible to obtain a set of readings for that displacement with the same degree of accuracy as was possible in the preceding sets.

The writer was unable to detect any asymmetry in the amount of acceleration of one component as compared to the corresponding retardation of the other. A cross hair was used in the observing telescope and the two sets of fringes were observed to shift symmetrically with respect to it.

The experiment just described was undertaken at the suggestion of Dr. D. B. Brace to whom the writer wishes to express his thanks for his interest.

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A HALF-SHADE ELLIPTICAL POLARIZER AND COMPENSATOR.

BY D. B. BRACE.

FRESNEL[1] has shown that the intensity of a beam of polarized light of unit amplitude, after passing through two double refracting plates and an analyzing nicol is given by the formula.

$$\begin{aligned}&\cos^2 s + \sin 2i' \sin 2a \cos 2(a + i' - s) \sin^2 \pi N' \\ &\quad - \cos 2i' \sin 2a \sin 2(a + i' - s) \sin^2 \pi N \\ &\quad - \sin 2i' \cos^2 a \sin 2(a + i' - s) \sin^2 \pi(N' + N) \\ &\quad + \sin 2i' \sin^2 a \sin 2(a + i' - s) \sin^2 \pi(N' - N)\end{aligned} \tag{1}$$

where the primes refer to the first plate, s is the azimuth of the final with the initial plane of vibration, i' the azimuth of the principal component of vibration in the first plate, a the azimuth of the principal vibration in the second plate with that of the first and N the differential order of the double refraction of the plates. If instead of a first plate of uniform thickness we suppose two in juxtaposition of different thicknesses but in the same azimuth, then, if the nicols are crossed, we have, as the condition for a match, since

$$s = 90^\circ \text{ and } i' = i'',$$

$$\begin{aligned}&- \sin 2i' \sin 2a \cos 2(a + i') \sin^2 \pi N' \\ &\quad + \cos 2i' \sin 2a \sin 2(a + i') \sin^2 \pi N \\ &+ \sin 2i' \cos^2 a \sin 2(a + i') \sin^2 \pi(N' + N) \\ &\quad - \sin 2i' \sin^2 a \sin 2(a + i') \sin^2 \pi(N' - N) \\ &= - \sin 2i' \sin 2a \cos 2(a + i') \sin^2 \pi N'' \\ &\quad + \cos 2i' \sin 2a \sin 2(a + i') \sin^2 \pi N \\ &+ \sin 2i' \cos^2 a \sin 2(a + i') \sin^2 \pi(N'' + N) \\ &\quad - \sin 2i' \sin^2 a \sin 2(a + i') \sin^2 \pi(N'' - N)\end{aligned} \tag{2}$$

[1] Oeuvres, T. 1, p. 624.

If i is the azimuth of the second plate $a = i - i'$. Substituting, the first term becomes

$$\begin{aligned} &- \sin 2i' \sin 2(i - i') \cos 2i \sin^2 \pi N' \\ &\qquad + \cos 2i' \sin 2(i - i') \sin 2i \sin^2 \pi N \\ &+ \sin 2i' \cos^2(i - i') \sin 2i \sin^2 \pi(N' + N) \\ &\qquad - \sin 2i' \sin^2 (i - i') \sin 2i \sin^2 \pi(N' - N). \end{aligned}$$

If now the plates are interchanged the intensity of the light will not be affected since, on interchanging the primes, we have

$$\begin{aligned} &- \sin 2i \sin - 2(i - i') \cos 2i' \sin^2 \pi N \\ &\qquad + \cos 2i \sin - 2(i - i') \sin 2i' \sin^2 \pi N' \\ &+ \sin 2i \cos^2 - (i - i') \sin 2i' \sin^2 \pi(N' + N) \\ &\qquad - \sin 2i \sin^2 - (i - i') \sin 2i' \sin^2 - (N' - N), \end{aligned} \tag{2a}$$

which is identical with the previous expression. The same will be true of the second member of (2). Hence the consequences to be deduced will be independent of the order of succession of the plates.

Expanding in (2) the sine and cosine, transposing and substituting $\sin^2 x - \sin^2 y = \sin (x + y) \sin (x - y)$ and dividing through by $\sin 2i'$ and $\sin \pi (N' - N'')$, since neither will be zero in our applications, we have

$$\begin{aligned} &(- \cos 2i' \sin 2a \cos 2a + \sin 2i' \sin^2 2a) \sin \pi (N' + N'') \\ &\qquad + (\cos 2i' \cos^2 a \sin 2a \\ &\quad + \sin 2i' \cos^2 a \cos 2a) \sin \pi (N' + N'' + 2N) \\ &+ (- \cos 2i' \sin^2 a \sin 2a - \sin 2i' \sin^2 a \cos 2a) \sin \pi (N' \\ &\qquad + N'' - 2N) = 0. \end{aligned} \tag{3}$$

In order to discuss the roots of this equation we will transform to the tangent form since it may take any value between $+\infty$ and $-\infty$. Substituting,

$$\sin 2a = \frac{2 \tan a}{1 + \tan^2 a}, \qquad \sin^2 a = \frac{\tan^2 a}{1 + \tan^2 a},$$

$$\cos 2a = \frac{1 - \tan^2 a}{1 + \tan^2 a}, \qquad \cos^2 a = \frac{1}{1 + \tan^2 a},$$

and collecting terms, we have

$$\tan^4 a\{-\sin 2i' \sin \pi[2N-(N'+N'')]\}$$
$$+\tan^3 a\{2\cos i' \sin \pi(N'+N'')+2\cos 2i' \sin \pi[2N-(N'+N'')]\}$$
$$+\tan^2 a\{4\sin 2i' \sin \pi(N'+N'')-\sin 2i' \sin \pi(2N+N'+N'')$$
$$+\sin 2i' \sin \pi[2N-(N'+N'')]\}$$
$$+\tan a\{-2\cos 2i' \sin \pi(N'+N'')+2\cos 2i' \sin \pi(2N+N'+N'')\},$$
$$+\{\sin 2i' \sin \pi(2N+N'+N'')\}=0. \qquad (5)$$

Dividing through by the coefficient of $\tan^4 a$ we see that the constant term is

$$-\frac{\sin \pi[2N-(N'+N'')]}{\sin \pi[2N+(N'+N'')]}.$$

In the physical applications the second plate and the mean of the first two will never be of a higher order than a quarter wave. We will, therefore, discuss the roots of this equation under the conditions that

$$N \gtrsim \tfrac{1}{4}, \text{ and } 2N+N'+N'' \gtrsim 1. \qquad (6)$$

The numerator of the constant term is positive and the denominator is positive, when $2N > N'+N''$, and thus, under the assumed conditions, this term is negative, and hence we know by the rule of signs that there are at least two real roots, one positive and the other negative, *i. e.*, we can always obtain a match in two different positions of the compensator. Thus, if we set the biplate in any azimuth whatever, we can always rotate the compensator into two positions that will give a match, and that too for any color of the spectrum which satisfies (6). If we make either N' or $N''=0$ we see that these conditions are not changed. In this case our biplate reduces to a plate of uniform thickness. This plate may cover one half the field of view or form a single strip — a "sensitive-strip" — for furnishing a sensitive system of comparison. Whatever its position, the compensator can always be set for a match in two positions for any color. For most purposes it will be preferable (for reasons given later) to set the biplate or strip in the position of greatest intensity, namely, at an azimuth of 45°.

Introducing the condition $i' = i'' = 45°$, the biquadratic reduces to the form

$$\tan^4 a\{-\sin\pi[2N-(N'+N'')]\}+\tan^2 a\{4\sin\pi(N'+N'')-\sin\pi[2N+(N'+N'')]+\sin[2N-(N'+N'')]\}+\sin\pi(2N+N'+N'')=0. \quad (7)$$

Put $A = \sin\pi[2N-(N'+N'')]$

$B = 4\sin\pi(N'+N'')-\sin\pi(2N+N'+N'')+\sin\pi[2N-(N'+N'')]$

$C = \sin\pi(2N+N'+N'')$.

Solving,

$$\tan^2 a = \frac{B \pm \sqrt{\Delta}}{2A}, \quad (8)$$

where the discriminant is

$$\Delta = B^2 + 4AC.$$

If we assume the condition $2N+N'+N'' \geqslant 1$, C will always be positive. If now $2N > N'+N''$, A will always be positive and hence Δ also. $\tan^2 a$ will then have two real roots. Since in this case $\Delta > B^2$, one of the roots will be positive and the other negative. Tan a itself will then have two imaginary roots and two equal real roots of opposite signs and hence a will have equal and opposite values. Thus there will be two settings of the compensator, in equal and opposite azimuths with respect to the first plate. It is needless to state that a rotation of the compensator through 180° will give the same settings. If now $2N < N'+N''$, A is $-$ and $\Delta < B^2$ and hence $\tan^2 a$ has two negative roots and consequently all the roots of tan a are imaginary and a impossible, *i. e.*, no position of the compensator will give a match. Thus if N be ever so little less than $(N'+N'')/2$ the physical problem will be impossible. When $2N = N'+N''$ one value of $\tan^2 a$ is 0/0, and will be found to be negative on taking the variation of the functions in the usual way, and the other is $+\infty$ and hence $\tan a = \pm\infty$ or $a = \pm 90°$. As $(N'+N'')/2$ decreases from the value N to 0, B approaches 0 and Δ therefore $4A^2$ so that in the limit $\tan^2 a = \pm 1$ and $a =$ becomes $\pm 45°$. Hence a may have any value between $\pm 90°$ and $\pm 45°$ under the conditions stated. When $a = 45°$ the principal axis of the compensator lies in the plane of vibration and consequently

produces no effect. Between these limits we have all the settings requisite for obtaining a match in any case of double refraction whatever. In the case $2N = N' + N'' = N'$ where $N'' = 0$, say, the plates are "crossed" and the equivalent thickness of the two plates is equal to that of the second plate, but rotated through an angle of 90°.

The sensibility of this system will depend, as in any photometric comparison, upon the uniformity of the intensity of the light in different portions of the field and upon the vanishing of the bounding lines when the intensities are the same. The first condition requires absolute uniformity in thickness and parallelism in the section, as well as constant angles of incidence for all rays. The second condition will be realized in proportion as the section is thinner. Hence this cannot exceed a certain limit nor can it be less than a certain amount in order that the expression for the intensity of the transmitted beam, discussed above, be great enough to ensure the greatest sensibility to the eye in judging of a match. The thickness of course will depend upon the requirements of the individual experiments, being conditioned by the available light, the absorption, reflection, etc., of the various arrangements. We may, however, reach an approximate estimate of the possibilities of such a system, where these factors do not seriously enter in, by comparison with data which we have in the case of the half-shade polariscope and the spectrophotometer.

With white light and a sensitive viewing screen with a vanishing line, settings can be made whose greatest difference will not exceed one half of one per cent. Moore[1] has attained this sensibility in the case of monochromatic light with a spectrophotometer for the mean spectral colors. With the half-shade polariscope and the use of a broad source of white light, without rotation, a setting to a thousandth of one degree is claimed. This however is never possible in practice where rotation occurs, which usually reduces the sensibility ten times or so, depending on conditions of light intensity, rotary dispersion, etc. Bates[2] has, however, attained with a sensitive-strip spectropolariscope a sensibility such that, for the mean colors of the

[1] PHYS. REV., Vol. 12, p. 161.
[2] Ann. d. Physik. (4), B. 12, p. 1096.

spectrum under rotary dispersion, the extreme differences of his readings were less than .007°. To express these results photometrically, it will be necessary to obtain a change in intensity represented by this quantity. In the half-shade system, we usually have two portions of the field whose planes of polarization make a slight angle 2θ with each other. If the intensity of the light from each portion is unity, the amount passing through the analyzer for a match, is

$$I = \sin^2 \theta. \tag{9}$$

The total change in I by a change $\partial\theta$ is

$$\partial I = 2 \sin \theta \cos \theta \partial\theta = 2\theta\partial\theta,$$

when θ is small as is usually the case.

The ratio of this to the original amount is

$$\frac{\partial I}{I} = \frac{2 \sin \theta \cos \theta \partial\theta}{\sin^2 \theta} = \frac{2\partial\theta}{\tan \theta} = 2\frac{\partial\theta}{\theta}.$$

This is the fractional change in one portion of the field and $-\partial I/I$ in the other produced by a rotation $\partial\theta$ and hence the relative change is

$$\frac{\partial I}{I} = 4\frac{\partial\theta}{\theta}. \tag{10}$$

Comparing this with our sensibiltty .005 in photometric comparisons we have

$$4\frac{\partial\theta}{\theta} \lessdot .005. \tag{11}$$

In the most favorable case mentioned $\partial\theta = .001°$. Hence, $4 \times 0.001° \div \theta \lessdot .005$ or $\theta \gtrdot .8°$ and $2\theta \gtrdot 1.6°$ must be the angle between the elements of the half-shade. The corresponding intensity of the field must be sufficient to give the eye the requisite degree of sensibility. This is rarely the case. However in polariscopic work it is not so much a question of specific photometric requirements as a maximum sensibility in testing rotations under given conditions. More usually where rotation occurs, $\partial\theta \gtrdot .01°$.

Thus $4\frac{0.01}{\theta} \lessdot .005$ or $\theta \gtrdot 8°$ or $2\theta \gtrdot 16°$.

This value of θ will usually make the intensity of the field such that the photometric sensibility of .005 may be attained. However, even with such a sufficient source, the scattered light from the polarizer may prevent its attainment. In the experiments of Bates

$$2\theta = 20.4', \ \delta\theta = .005°,$$

approximately.

Thus
$$4\frac{\delta\theta}{\theta} = 4\frac{0.3'}{10.2'} = .117,$$

or about one twenty-third the normal light sensibility, and yet this was the photometric requisite to give him the highest rotary sensibility with the available light intensity. These results will serve for comparison with those obtained from elliptic polarization with half-shade systems, the photometric and polariscopic conditions of which are practically identical.

For the sake of simplicity, let us consider — what will usually be the most effective system in practice — the first plate of uniform thickness and consisting either of a strip in the middle of the field of view or covering one side of it. Let its azimuth be 45°. Then the second member of (2) becomes, on making the substitutions, $N' = 0$, $2i' = 90°$, $\theta = a - 45°$ where θ is the azimuth of the second plate with the plane of vibration.

$$\begin{aligned} I &= (\sin^2 a - \cos^2 a)\cos 2a \sin^2 \pi N = \cos^2 2a \sin^2 \pi N \\ &= \sin^2 2\theta \sin^2 \pi N \qquad (12) \\ \therefore \delta I &= 4 \sin 2\theta \cos 2\theta \sin^2 \pi N \delta\theta. \end{aligned}$$

Hence
$$\frac{\delta I}{I} = \frac{4 \sin 2\theta \cos 2\theta \sin^2 \pi N}{\sin^2 2\theta \sin^2 \pi N}\delta\theta = 4\frac{\delta\theta}{\tan 2\theta} = 2\frac{\delta\theta}{\theta} \qquad (13)$$

when θ is small.

To determine the corresponding change in the other portion it would be necessary to differentiate the first member of (2) and then substitute the roots of the biquadratic (7). This would give too complicated an expression for interpretation; but we may obtain an approximate solution in a different way. Let x and y, $\sin\theta$ and $\cos\theta$ be the component vibrations and amplitudes. The resulting elliptical vibration referred to its center, is

$$\frac{x^2}{\sin^2\theta}+\frac{y^2}{\cos\theta^2}-\frac{2xy}{\sin\theta\cos\theta}\cos 2\pi N=\sin^2 2\pi N. \qquad (14)$$

In the first plate $i'=45°$, and $\cos^2\theta=\sin^2\theta$ and hence the axes of the vibration make an angle of $45°$ with the axis of the crystal. Since $N'>\frac{1}{4}$ the major axis is parallel to initial direction of vibration. The ratio of the semi-minor axis to the semi-major axis is

$$\frac{a}{b}=\sqrt{\frac{1-\cos 2\pi N'}{1+\cos 2\pi N'}}=\tan \pi N'. \qquad (16)$$

If we rotate the coördinate axes in (14) through an angle δ and equate the coefficients of xy to zero, we have

$$\tan 2\delta=\cos 2\pi N\tan 2\theta, \qquad (17)$$

which gives the angle between the y-axis and the major axis of the ellipse.

Equation (17) shows that if $N=1/4$, $\delta=0$, that is the major axis always coincides with the y-axis of the crystal. Thus if we rotate the plate from azimuth $45°$ to $0°$, the axes of the ellipse move through the same angle. If $0<N<\frac{1}{4}$, $\delta=45°$ for $\theta=45°$, that is the major axis of the ellipse lies in the plane of vibration. If $0<\theta<45°$ the major axis will lie between the y-axis or the principal axis of the plate and the plane of the initial vibration when it is rotated. If N is small the azimuth of the major axis will remain zero as the plate is rotated and we may use (16) for the approximate ratio of the axes. Within this limit, such a plate is equivalent in its different azimuths to plates of corresponding orders in zero azimuth. The ratio of the axes of an elliptical vibration is by (16) $\tan \pi N$. When $N=1/4$ this ratio is

$$\frac{\sin\theta}{\cos\theta}=\tan\theta=\tan\pi N \text{ or } N_1=\frac{\theta}{\pi} \qquad (18)$$

when θ is small, where N_1 is the equivalent order in azimuth θ. N_1 is the equivalent order of a quarter-wave plate corresponding to a plate in zero azimuth. From (16)

$$\frac{a_1'}{b_1'}:\frac{a_1}{b_1}=\pi N_1':\pi N_1,$$

but for the same azimuth

$$\frac{a_1'}{a_1} = \frac{N'}{N},$$

and therefore

$$\frac{N_1'}{N_1} = \frac{N'}{N};$$

but

$$N_1 = \frac{\theta'}{\pi},$$

and thus

$$N_1' = \frac{\theta'}{\pi}\frac{N'}{N}, \tag{19}$$

and hence if

$$N_2 = \frac{\theta}{\pi} = N_1',$$

$$\frac{\theta}{\theta'} = \frac{N'}{N} = \frac{N_1'}{N_1}. \tag{19a}$$

In practice it is convenient to use a compensating plate of low order, say $N_1 < \frac{1}{50}$ and then an auxiliary quarter-wave plate for greater retardations, so that the approximate equations (18), (19) and (19*a*) can be used. This plate should really be of the order $\frac{1}{4}$ for the shortest waves required and then its order, for any other wave-length used, determined by means of differential dispersion after the method of channeled spectra [1] and then by means of equations (19) and (19*a*).

Returning now to the discussion of (12) and (13), it had already been shown from (8) that when $2N = N' + N''$, or when

$$N = \frac{N'}{2},$$

in the present case, there was a match and the plates were "crossed." Thus for a match the combination must be equivalent to a "crossed" system of equal order.

Equation (13) shows that, for the portion of the field covered by the second plate only, a positive increment in θ gives a positive increment in I. Since now we have shown that the two plates cover-

[1] Phil. Mag., Oct., 1899. Also Rendtorff, Phil. Mag., May, 1901.

ing the outer portion of the field are equivalent to the first plate "crossed" (or turned through 90°), to maintain the match we must suppose the equivalent system turned in the opposite direction through an angle $-\delta\theta$, so that for the second portion of the field

$$\frac{\delta I}{I} = -2\frac{\delta\theta}{\theta} \qquad (13a)$$

approximately. If now a system of unknown order be inserted, at an azimuth of 45° in the path of the ray causing N or $\sin \pi N$ to change, a variation of $\sin 2\theta$, or of 2θ, when small, in inverse ratio will compensate the effect and I will be kept constant and the match maintained. The phase change may be obtained by noting the rotation of the compensator and calculating from (18) or (19), knowing the constants of the system.

The restriction in the use of the compensator within the limits of the optical sensibility of 1/200 or within whatever fractional change the eye can detect under the particular conditions imposed upon the system, can be calculated from (12). Thus if the order of the unknown plate is N_2 and such that $\sin^2 \pi N_2 = \sin^2 2\theta \sin^2 \pi N$ so that the match is not disturbed, the error will be in taking 2θ in place of $\sin 2\theta$. The error may be obtained by expanding the sine, which gives

$$4\theta^2 - \sin^2 2\theta = \tfrac{16}{3}\theta^4 + . \qquad (20)$$

But

$$\tfrac{16}{3}\theta^4 \div 4\theta^2 \gg \tfrac{1}{200}, \quad \therefore \theta^2 \gg .00375 \quad \text{or} \quad \theta \gg 3.5°$$

approximately. If the sensibility is $\frac{1}{500}$, $\theta^2 \gg .015$ or $\theta \gg 9°$ approximately. This range of the compensator may be slightly different on account of the presence of the second plate, but is independent of the order of the compensating plate. For large orders of the unknown plate the sine must be used instead of the angle.

From (13) and (13a) we obtain as the relative change of intensity

$$\frac{\delta I}{I} = 4\frac{\delta\theta}{\theta}, \qquad (21)$$

which is the same as (10), the equation of the half-shade polariscope. Thus if 1/200 is the sensibility of the eye

$$4\frac{\delta\theta}{\theta} \ll .005.$$

When θ is small we have from (18) and (19)

$$\frac{\delta I}{I} = 4\frac{\delta\theta}{\theta} = 4\frac{\delta N_1}{N_1} \lessdot .005. \tag{22}$$

Hence the sensibility will depend upon how small a value of N_1 may be used and still give sufficient intensity for the maximum sensibility of the eye; and the availability of this value in practice will also be restricted by the mechanical and optical conditions. Sections have been obtained of order 1/700 for green light, but it is doubtful if sections of any natural double refracting material can be obtained of an order much less than 1/1,000. With direct sun light the intensity is sufficient for comparisons. Assuming this value of N' for the first plate or strip, the equivalent order of the compensating plate would be $N_1 = .0005$. Hence we have

$$4\frac{\delta N_1}{.0005} \lessdot .005 \text{ or } \delta N_1 \lessdot 6.2 \times 10^{-7} \tag{23}$$

as the limiting value of the change of phase, which could be observed under the most favorable conditions with an azimuth of 45°. If the azimuth of the strip is diminished this limit of sensibility may also be increased indefinitely; but for reasons given further on the photometric conditions are not maintained and it is doubtful if this sensibility could be increased. This is about fifty times greater than has been obtained with this same system using plates about ten times as thick, but even this latter is far beyond that of other methods heretofore used. We may compare the intensity of light in this system with that which has been found practicable in the polariscope. In the polariscope (9) gave

$$I = \sin^2\theta.$$

In this system

$$I = \sin^2 2\theta \sin^2 \pi N_1 = \sin^2 \pi N_1,$$

since

$$\theta = 45°.$$

In the experiments of Bates

$$\theta = 10.2' \text{ and } I = \sin^2 10.2'.$$

In the present instance

$$N_1 = .0005 \text{ and } \pi N_1 = 5.4',$$

and we have

$$I = \sin^2 5.4'.$$

This shows that with proper refinements in the optical system, monochromatic light can be used with this order ($N_1 = .0005$) which is also about the limit of the crystalline sections. Of the most available crystals — Iceland spar, quartz, selenite and mica — the latter is the only one from which such thin sections can be obtained. In spar $N = 300$ for 1 mm. thickness approximately, and hence for $N' = .001$ the thickness would have to be .000003 mm., and this thickness could not vary by more than .005/4 of itself to give uniform intensity over the field. This of course is utterly unattainable by any process of grinding. For quartz and selenite $N = 15$ for 1 mm. approximately. The thickness here could be twenty times as great, but this is about the limit of correction alone in a "flat" several millimeters thick. The cleavage of selenite to this degree has not thus far been found possible. For mica the thickness could be nearly double this value and hence its cleavage is practicable. The possibility of such a thin section was suggested to the writer several years ago in preparing the mica retardation plate used with the prism in the resolution of the Faraday "effect" into the circular components.[1] It was noticed that very small thin laminæ occasionally adhered to the section which was being split off and which gave, when observed directly with the eye, the characteristic tints in Newton's interference scale. After some weeks' attempts, sections, occasionally several square centimeters in area, could be obtained of uniform tint in the lesser orders of this scale. More usually these sections gave several tints with very sharp and almost vanishing bounding lines, exactly the optical condition required. Smaller strips were occasionally obtained giving as low as the first violet in Brücke's[2] corrected scale, or a thickness of only about .00017 mm. These films were very delicate and might have small holes in them, resulting from imperfect cleavage, which destroyed their efficiency when introduced into the field of view. These were mounted between the thinnest cover-glasses, which had been tested out for double refraction, with Canada balsam whose

[1] Phil. Mag., April, 1901, p. 472.

[2] Pogg. Ann., B. 88, p. 363; Mascart, Optique, T. 1, p. 210.

index was the same as the mean of that of mica and which would hence make the section practically invisible and thus give, further, a vanishing line at the boundary. These were frequently torn or were flowed out in the process of cementing on account of the impossibility of seeing them. With proper care and patience suitable compensator films and sensitive strips can readily be obtained from ordinary mica and mounted for the purposes mentioned.

Equation (12) gives for $\theta = 45°$, $I = \sin^2 \pi N_1$, the intensity of the incident polarized light, being taken equal to unity. If we call A^2 the intensity for any color, then ΣA^2 represents white light and we have

$$[I] = \Sigma[A^2 \sin^2 \pi N_1]. \tag{25}$$

Poisson's equation for light reflected normally from a thin plate reduces, for ordinary glass, to

$$I = \left(\frac{2\rho}{1-\rho^2}\right)^2 A^2 \sin^2 2\pi N,$$

where N is the order of interference. For white light we have

$$[I] = \left(\frac{2\rho}{1-\rho^2}\right)^2 \Sigma[A^2 \sin^2 2\pi N]. \tag{26}$$

Here N, the absolute order, corresponds to N_1, the differential order of double refraction of the plate. Thus a thin plate of order N will give the same tint by reflected light as a crystalline section of differential order N_1 gives by transmission with the nicols crossed. In three plates used the differential order N_1 had the values $\frac{1}{75}$, $\frac{1}{100}$, $\frac{1}{700}$ respectively; thus for the same absolute orders, the equivalent air thickness would be .0005 mm., the wave-length of green light, multiplied into these fractions or 6.7 $\mu\mu$, 5 $\mu\mu$, .7 $\mu\mu$. The lowest order in Brücke's table is 40 $\mu\mu$ = iron gray. With the very lowest orders white light may be used without obtaining any trace of coloration in the field of view. But higher orders, which, with fairly intense light, give no perceptible coloration, do show tint with increased intensity, as with sun light. On account of the tint and the greater prominence of the bounding line, thicker strips are not as satisfactory in intense light. Such strips, instead of being placed in an azimuth of 45°, may of course be rotated into a position of

less azimuth and thus give an equivalence to a thinner section, but the vanishing of the line is less complete and the compensation of all colors less satisfactory. Hence it is necessary to use corresponding compensator sections and the thinnest sensitive strips possible with the available intensity of light and the conditions of greatest sensibility to the eye. Were it possible to cut these thinner crystalline sections and mount them "crossed" and in juxtaposition so as to obtain a completely vanishing line, the compensation might be more perfect and the coloration, if there be any, less evident than in the arrangement here described. But such a system seems unrealizable and in actual results far below the sensibility obtained with natural cleavage termini. These can usually be obtained sufficiently regular and straight for all comparison work. In fact, as frequently happens, sections of slightly different thickness in different portions give exactly that change in intensity in various parts of the field requisite for realizing the "contrast principle" in photometric comparisons. Thus, in a certain section, a portion was of order $\frac{1}{100}$ and another portion of order $\frac{1}{100} + \frac{1}{700}$ and so on. This occurred occasionally also in the very lowest orders. Instead of using such a section to realize "constrast" it could be mounted so as to make this bounding line the "vanishing" line of the fields to be compared, thus giving an equivalent to a sensitive-strip of order $\frac{1}{700}$ say. This, however, is not advisable if strips of this order can be obtained directly, since, as already mentioned, the thinner the section the more satisfactory the settings, because of the more complete vanishing of the bounding line and of the coloration when white light is used. If a strip were rotated from an azimuth of 45° into a less azimuth, any intensity could be obtained, but this was found not so satisfactory in color or in the vanishing line as a thinner strip of the same equivalent order.

Within certain limits, the second plate serves the double purpose of not only giving a half-shade combination with a vanishing line for making comparisons, but of compensating for any change of phase produced on the ray. For white light the thickness is restricted in the same way as the strip is limited to the first orders in Brücke's scale. Hence the compensation possible in this way is confined to the smaller orders. The method of compensation by

rotating a plate in this way is also not generally applicable, even with homogeneous light, to the larger orders, since the intensity of the light is too great to obtain the highest sensibility in a setting for a match.

The sensibility attained with this system in actual practice compares very favorably indeed with other systems already in use. The highest sensibility available in each system was not attempted, but only that which could be conveniently obtained with ordinary precautions and under like conditions for each system. A support carrying the polarizing and analyzing nicols was arranged so that the various elements of the different systems to be compared could be inserted in the path of the ray. An acetylene flame placed before the polarizer was generally used to illuminate the system. Green glass could be placed in front of this for approximately homogeneous light tests. Immediately after the polarizing nicol, whose principal plane made 45° with the vertical, came the compensator, then the sensitive-strip, each mounted on a collar which fitted the tube containing the nicol. The collar of the latter carried a divided arc and that of the former a pointer. Next came a vertical graduated circle upon which could be mounted any plate to be compared, usually a quarter-wave plate. Then followed a vertical strip of crown glass 13 mm. wide and 2 mm. thick upon which was cemented a cover glass for receiving weights. Then came a horizontal glass strip with a clamp for producing flexure, and immediately in front of this a micrometer screw carrying two horizontal wires, a millimeter or two apart. Thirty to 50 centimeters beyond this came the analyzing nicol and circle and a short focus observing telescope. In this space could be inserted the various other pieces to be compared, such as quartz compensator, glass cubes, etc. The order of the quarter-wave mica plate was determined by means of a selenite wedge in the usual way and found to be of that order for green light $\lambda = .0005$ mm. approximately. With these elements thrown out of the field of view, the nicols were crossed. The sensitive-strip, compensator and quarter-wave plate were then thrown in and out successively and the reading for zero azimuth of each recorded. The sensitive-strip was then thrown in at an azimuth of 45°, then the compensator so

as to give a match. Successive settings of the latter were then made on each side of this position where the eye could just detect a change in intensity at the vanishing line. This was now repeated with the green glass before the polarizer. With the particular system used a setting to within 0.1° with white and 0.2° with green light could be made. By means of (18), (19) and (19a) this sensibility can be expressed in terms of the relative retardation of the component rays. Thus with the sensitive-strip in an azimuth of 45° a match was obtained by means of the quarter-wave plate for $\theta = 56'$, which gives the equivalent order $N_1 = \frac{56}{60} \times \frac{1}{180} = \frac{1}{200}$ approxmimately. But it was proven that $N = \frac{1}{2}(N' + N'')$ so that here $N_1' = \frac{1}{2} N'$ or the order of the strip $N' = \frac{1}{100}$ for $\lambda = 500\mu\mu$ approximately. Replacing the quarter-wave plate by the compensating plate, setting for a match and rotating the same through 5°, and then introducing the quarter-wave plate, the latter gave a match again in azimuth 16′. Hence from (19a) the order of the compensator is $N = \frac{16}{800} \times \frac{1}{4} = \frac{1}{75}$ approximately. Thus the retardations corresponding to 0.1° and 0.2° on the compensator are

$$\frac{0.1}{5} \times \frac{16}{60} \times \frac{\lambda}{180} = \frac{\lambda}{34{,}000} = 3 \times 10^{-5}\lambda \text{ and } 6 \times 10^{-5}\lambda \text{ respectively.}$$

The former is fifty times the limit given in (23). From (22) $4\frac{\partial\theta}{\theta} < .005$. The azimuth of the quarter-wave plate to match the strip was $\theta = 56'$. The equivalent sensibility on this plate would be $\partial\theta = {}^\circ \times 0.1\frac{4}{75}$. Hence

$$4\frac{\partial\theta}{\theta} = 4\frac{0.4 \times 60}{75} \times \frac{1}{56} = .023$$

as against .005, the normal sensibility. This result indicates how well the optical conditions of uniformity of field and of a vanishing line are fulfilled by these thin sections of mica. Two settings of the compensator at 6.°5 and 13° corresponded to a proportionate rotation of the quarter-wave plate showing the proportionality within this range. Another section of mica which was among the thinnest obtained, gave a match with the quarter-wave plate in an azimuth of 8′. Hence the equivalent order of the quarter-wave plate was

$N_1 = \frac{8}{60} \times \frac{1}{180} = \frac{1}{1350}$, and the order of the strip $\frac{1}{675}$ approximately. In another section of two different thicknesses, a rotation of 8′ by the quarter-wave plate was necessary to pass from a match of one to the other. Hence the difference in orders was $N'' - N' = \frac{8}{60} \times \frac{2}{180} = \frac{1}{675}$ approximately. The sensibility of the method in comparison with others under similar optical conditions was readily obtained by introducing the various systems already mentioned. Bravais' "sensitive-tint" biplate when placed in the path of the ray showed a change of tint between the two halves of the field with a turn of 1° of the quarter-wave plate. This corresponds to a change of phase of $\frac{\lambda}{180}$ which is only about $\frac{1}{200}$ the sensibility obtained above with the sensitive strip system under the same conditions of illumination. Undoubtedly with a different intensity and more careful adjustment a higher sensibility could be obtained with not only Bravais' biplate but also with this system. In fact Bravais [1] with intense light could detect 0.7° rotation of the quarter-wave plate or $\frac{\lambda}{250}$.

The comparison with the shift of a black band was made by inserting the vertical strip, the horizontal strip and the micrometer already mentioned. The sensibility of this system depended on the amount of flexure and varied considerably. Thus with a flexure, such that the band was quite sharp and distinct, 500 gms. on the vertical strip gave a reading on the micrometer screw of 36, while the least shift of the screw which could be detected was 12. On reducing the flexure until the black band was hardly visible 200 gms. gave 23 divisions while 100 gave 11 divisions as near as could be observed. This represented the sensibility. With 200 gms. a match was obtained with the compensator on rotating 2.5°. Since 0.1° was the sensibility, this would correspond to 8 gms. or a sensibility 12.5 times that with the black band. Under more favorable conditions both systems would have given a greater sensibility, but this represents approximately the relative sensibility. Rayleigh,[2] using a lime-light and a black band, obtained 25 gms, as his sensi-

[1] Pogg. Ann., 96, p. 402.
[2] Phil. Mag., Dec., 1902.

bility. With crossed nicols alone, he obtained a sensibility over four times less, which would correspond to about fifty times less than that with the strip under similar conditions, a result approximately obtained by direct comparison. The compensators of the Babinet type would fail to give the sensibility of the single band obtained with the glass strip under flexure, since the bands are much narrower and sharper and hence less sensitive as shown above.

The method of Senarmont of using a quarter-wave plate or a Fresnel rhomb is of the same order of sensibility as the crossed nicols. Thus with green light 1,000 gms. on the vertical strip could not be detected, while the sensibility of the strip was 0.2° or 25 gms., or at least forty times greater. The double refraction in the Fresnel rhomb was so great that it could not be used with it at all to this degree of sensibility. A very slight pressure of the finger on a strip of glass at once showed marked contrast in the half shade. A fine quartz compensating wedge some 80 millimeters in length and ground very accurately from a differential order 0 up to 1 with compensating plate and wedge after the method of Soleil was found utterly useless to this degree of sensibility owing to the unavoidable double refraction in its glass mount. The application of a glass cube as a compensator under varying pressures as used by Bravais and by Wertheim is also subject to the same difficulty of initial strain. Only thin strips of glass are sufficiently free from strain to give an extended field of uniform intensity.

When the phase change is a function of the wave-length, as is usually the case, large retardations of different wave-lengths may be obtained by setting for a match and then varying the wave-length of the ray until a match again occurs for the next succeeding color and so on. This would represent a loss or a gain of half an order and, as in this way the full sensibility could be maintained and the portion of the spectrum or mean wave-length accurately determined, the error in the observations could be reduced to that calculated above.

Other methods of obtaining a vanishing line were tried without success. Thus by silvering a strip on the reflecting surface of a total reflecting prism, a vanishing line was obtained together with elliptically polarized light from the incident plane polarized light as

Fresnel and Brewster have shown. As the elliptical vibrations in each portion of the field were in the same direction but of different excentricities so that a match was possible, the changes in intensity in the two portions of the field were in the same direction, a condition contrary to a true half-shade instrument. The double refraction in the prism itself was an insurmountable difficulty.

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THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS IN METHYL ALCOHOL IN THE NEIGHBORHOOD OF THEIR CRITICAL POINTS. II.

By Charles A Kraus.

Discussion of Results.

As already stated, solutions in methyl alcohol exhibit a maximum of electrical conductivity which in round numbers, lies a hundred degrees below the critical point. This phenomenon was studied more carefully only in the case of potassium iodide and ammonium chloride. Even in these cases particular care was not observed, the results being obtained incidentally. However it will not be out of place to point out here a few facts that present themselves. The results are plotted in Fig. 2. The high value of the conductivity which these solutions possess beyond the critical point compared with that of such solutions as have been measured in sulphur dioxide and ammonia[1] is very striking. The fact impresses itself upon one that the comparison of the conducting power of different solvents by a comparison of the conductivity of their solutions at ordinary temperatures is somewhat arbitrary. The conductivity of a solution is a function of its temperature and it is difficult to say what temperatures are to be looked upon as corresponding temperatures. Certainly we should take into account the distance from the critical point, for in any particular solvent this is in a large measure determinative of the conductivity. Viewed in this light the alcohols approach water much more nearly in the conducting power of their solutions than do either sulphur dioxide or ammonia. How they would compare with other solvents which have not been particularly studied in relation to their maxima of conductivity can not now be said.

The maxima also show some characteristic relations in regard to the behavior of different dissolved substances. It will be noticed

[1] A. Hagenbach, l. c.; P. Eversheim, l. c.

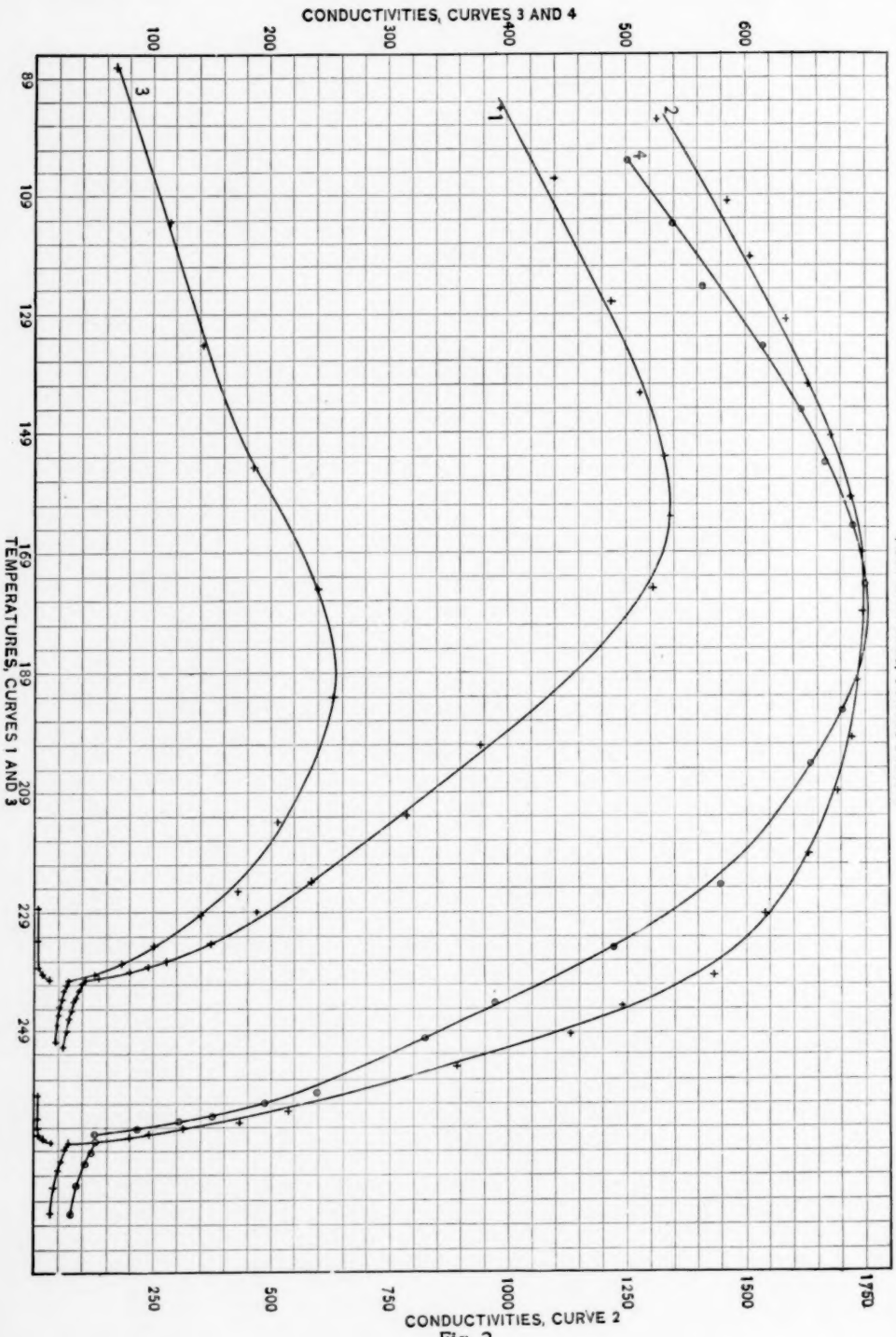
CONDUCTIVITIES, CURVES 3 AND 4
100
200
300
400
500
600
89
109
129
149
169
189
209
229
249
TEMPERATURES, CURVES 1 AND 3
3
1
2
4
64
84
104
124
144
164
184
204
224
244
TEMPERATURES, CURVES 2 AND 4
250
500
750
1000
1250
1500
1750
CONDUCTIVITIES, CURVE 2

Fig. 2.

that the curve for ammonium chloride, Curve 2, Fig. 2, much flatter than that for potassium iodide. In consulting the curves obtained by Franklin and Kraus for the same substances in ammonia it will be seen that there too the same difference exists. The relative positions of the maxima also bear much the same relations to each other in the two solvents. In the region just before the critical point is reached the ammonium chloride decreases in conductivity much more rapidly than potassium iodide. The concentration seems to have considerable influence on the position of the maxima as is apparent by comparing curves 1 and 4.

The curves studied in alcohol exhibit a constant direction of curvature until the critical point is reached, when the curvature is to the other side. The curves studied by Hagenback[1] exhibit the same peculiarity. All the curves studied by Franklin and Kraus[2] in ammonia exhibited this same behavior. Yet this is not a general property of electrolytic solutions as is seen on consulting the curve given by Franklin and Kraus[3] for potassium iodide in methylamine. In this solution the curvature turned away from the axis long before the critical temperature was reached. The curve tends to approach the axis of temperatures asymptotically. Just what would happen at the critical point in a solution of this kind it is impossible to predict. Some curves studied by Walden and Centnerszwer,[4] in sulphur dioxide exhibit the same peculiarity.

Curve 3 illustrates the reaction which takes place when a solution of potassium iodide is heated up. It is seen that already at a temperature of 140° reaction sets in, as is shown by the upward turn of the curve. Owing to this reaction the maximum lies at a much higher temperature than it otherwise would. In curve 3 the tube contained the same quantity of solute as in 1, the quantity of solvent had been somewhat diminished. In the neighborhood of 235° the reaction is complete as can be seen by comparing the values of $S \cdot V_1 V \times 10^6$ in series V. and VI.

The curve between conductivity and temperature is of great interest in the immediate neighborhood of the critical point. If, as

[1] Hagenbach, l. c.
[2] Franklin and Kraus, l. c.
[3] Franklin and Kraus, l. c., p. 90.
[4] Walden and Centnerszwer, l. c., p. 555.

much evidence goes to show, we may have present at the critical point two molecular species;[1] then it is to be expected that the change of the conductivity will be largely influenced by the relative quantities of these species present, throughout the region in which they may exist together. A number of measurements with U-tubes, some of which were constricted at the bend, showed great differences of density, existing between different parts of the solution. As nearly as could be judged the relative density of the gaseous to the liquid portion of the tube was in the ratio of 1 to 2. It is to be borne in mind that methyl alcohol is an associated liquid, so that what applies to methyl alcohol does not necessarily apply to other liquids.

Indeed the work of Ramsay and Shields[2] makes it very probable that association may continue beyond the critical point. Certainly as near the critical point as we are justified in applying the formulæ, the association possesses considerable values. Whether the association is the only factor that leads to non-homogeneity beyond the critical point, or whether another factor enters such as De Heen and others have noticed in non-associated liquids may well be left an open question until the disputed points in connection with non-associated liquids have been settled. As will be shown below, solutions in methyl alcohol may be far from homogeneous beyond the critical point, if properly treated. To explain this, however, in the case of an associated liquid offers no particular difficulty and it will be unnecessary to make any further assumptions unless collateral evidence makes it desirable. The results observed by Eversheim[3] in ammonia may likewise be due to association since ammonia[4] is an associated liquid.

However, the phenomena as observed in methyl alcohol do not exhibit any essential differences from other liquids that have been investigated in this direction. Again, in the methyl alcohol there was present solute in the liquid and a certain amount of gas in the

[1] An excellent résumé of the work done in this direction together with the reference is given by J. Traube, Ann. der Phys., 8, p. 267, 1902; Traube and Teichert, Ber. d. Deut. Phys. Ges., No. 13, p. 235, 1903; E. Mathias, Jour. d. Phys., 2, p. 172, 1903.

[2] Ramsay and Shields, Zs. f. Phys. Chem., 12, p. 433, 1893.

[3] Eversheim, Phys. Zs., June 15, p. 503, 1903.

[4] Franklin and Kraus, Amer. Chem. Jour.

vapor. But it is to be noted in this connection that the quantities of these disturbing elements present did not give rise to any appreciable changes in the observed phenomena. In one case the vapor space was filled with hydrogen. The phenomena suffered no change. It is possible to explain the phenomena in methyl alcohol by assuming an association of the liquid, yet this does not necessarily exclude the possibility that the observed phenomena are characteristic of the change from the liquid to the gaseous state. For the present this question is best left open.

The differences that may arise in the tube due to different treatment as regards stirring are well illustrated by the following experiments. A tube was heated up without stirring to 0.2° below the critical point, *i. e.*, by heating the tube 0.2° higher the meniscus disappeared in the usual way. The volume occupied by the liquid at this temperature was 0.38 of the total volume of the tube. On inverting the tube once or twice the liquid disappeared entirely and an unsaturated vapor was the result. In another case the same solution was heated 3.2° above the critical point. The specific conductivity of the solution at this temperature was 94.94×10^6. The volume of the liquid at the critical point was 0.36 of the total volume of the tube.

This measurement was carried out with the solution of series XIII. In series II. the same tube was used with the same quantity of solute but with a quantity of solvent which just filled the tube at the critical point. At 3.2° above the critical point II. gave $S = 35.00 \times 10^6$. Now in the two cases we have the same quantity of solute, only in the first case the solute is contained in 0.36 of the total volume of the tube, while in the second case the solute was distributed through the entire volume of the tube. Saying that the solute in the first case was contained in 0.36 of the volume of the tube means that at the critical point the liquid occupied 0.36 of that volume and, since the volume below the critical point changed in this case but very little with the temperature, this assumption seems justified. In order to compare the conductivities in the two cases, it is necessary that the solute be distributed in the same space. If on increasing the dilution there were no change in the conductivity owing to the change in dissociation, then one might

make the correction by multiplying the specific conductivity in the first case by the ratio (0.36) of the volumes in the two cases. This gives $S \cdot V_t / V \times 10^6 = 34.34$. In truth, the conductivity of alcohol solutions changes but very slowly with the dilution. Therefore the above corrected value of the conductivity in the first case should be very nearly the same as that in the second case if the properties of the solution in the first case are the same as in the second case. Now the corrected value in the first case is 34.34 against 35.00 in the second case. As regards the conductivity then, a solution, which, if properly mixed would form an unsaturated vapor solution before the critical point is reached, possesses, by virtue of non-homogeneity, arising from want of mixing, the same properties as a homogeneous solution which entirely fills the tube at the critical point. So long as the solution present be in liquid form on passing the critical point, it matters not what may be the other conditions under which it now exists; as regards the conductivity its properties are the same as those of a tube which at the critical point is homogeneously filled with liquid, provided sufficient time has not elapsed to efface the non-homogeneity by diffusion. For example, the pressure in the tube in the two cases must have been very different. The pressure then can have no considerable influence on the conductivity.[1]

On inverting the tube in series XIII. the conductivity fell to 5.2. The following may make clear what actually happened. A certain solution whose volume was 0.36 of the total volume of the tube had a specific conductivity of 94.94×10^6. If this solution was diluted with solvent which was in the liquid state as it passed the critical point, then the specific conductivity fell to 35.00 or the molecular conductivity increased in the ratio of 34.34 to 35.00 on diluting the volume of the solution from 0.36 to 1. If, on the other hand, the solution was diluted to the total volume of the tube, with solvent which was in the vapor state as the critical point was passed, then the specific conductivity fell from 94.94×10^6 to 5.2×10^6 or the molecular conductivity the dilution was decreased by the dilution in the ratio of 5.2 to 34.34. Depending therefore on whether the diluting solvent was in the liquid or the gaseous state

[1] Compare Hagenback, l. c., Ann. der Phys., 5, p. 305, 1901.

as it passed through the critical point, at a temperature 3.2° above the critical point the molecular conductivity was increased in the ratio of 34.34 to 35.00 or it was decreased in the ratio of 34.34 to 5.2 in diluting the volume of the solution from 0.36 to 1. It is conclusively shown then that the conductivity of a solution beyond the critical point is determined in a large measure by the quantity of liquid present as the critical point was passed, the tube not having been stirred since the passing of the critical point.

It still remains to determine if there is any change in the properties of either a liquid or a gas as the critical point is passed. As already pointed out this cannot be done with a tube that contains a mixture of liquidogenous and gasogenous molecules,[1] for the reason that we may have a change from one molecular species to another, a change which, in view of the different conducting power of the two species, would in all probability mask any change going on in either of the species alone. We must accordingly simplify the phenomenon by taking a tube which is as nearly as possible filled with a single species. To fill the tube with liquidogenous molecules it is only necessary to use a tube which is filled with liquid at the critical point. Series II. gives the results in such a case and the same are represented graphically in curve 9. As may be seen, the conductivity is a linear function of the temperature just below the critical point. Just beyond the critical point the conductivity is again very nearly a linear function of the temperature. It is apparent that at the critical point there is a sudden change in the tangent to the curve, indicating an abrupt change in property of the liquid as the liquid passes the critical point. In the curve plotted the conductivities are corrected for the volume. If such correction had not been made the change at the critical point would seem much greater. The question might arise if the result observed is not the result of a change brought about by the circumstance that at this point the volume ceases to change? This will indeed affect the results. The correction applied is on the basis of constant degree of dissociation. As a result of the change in volume the

[1] In the course of the paper, when for the sake of convenience use is made of the terms liquidogenous and gasogenous molecules, it should be remembered that they are applied here to an associated liquid and that they are not necessarily identical with the same terms as applied to non-associated liquids.

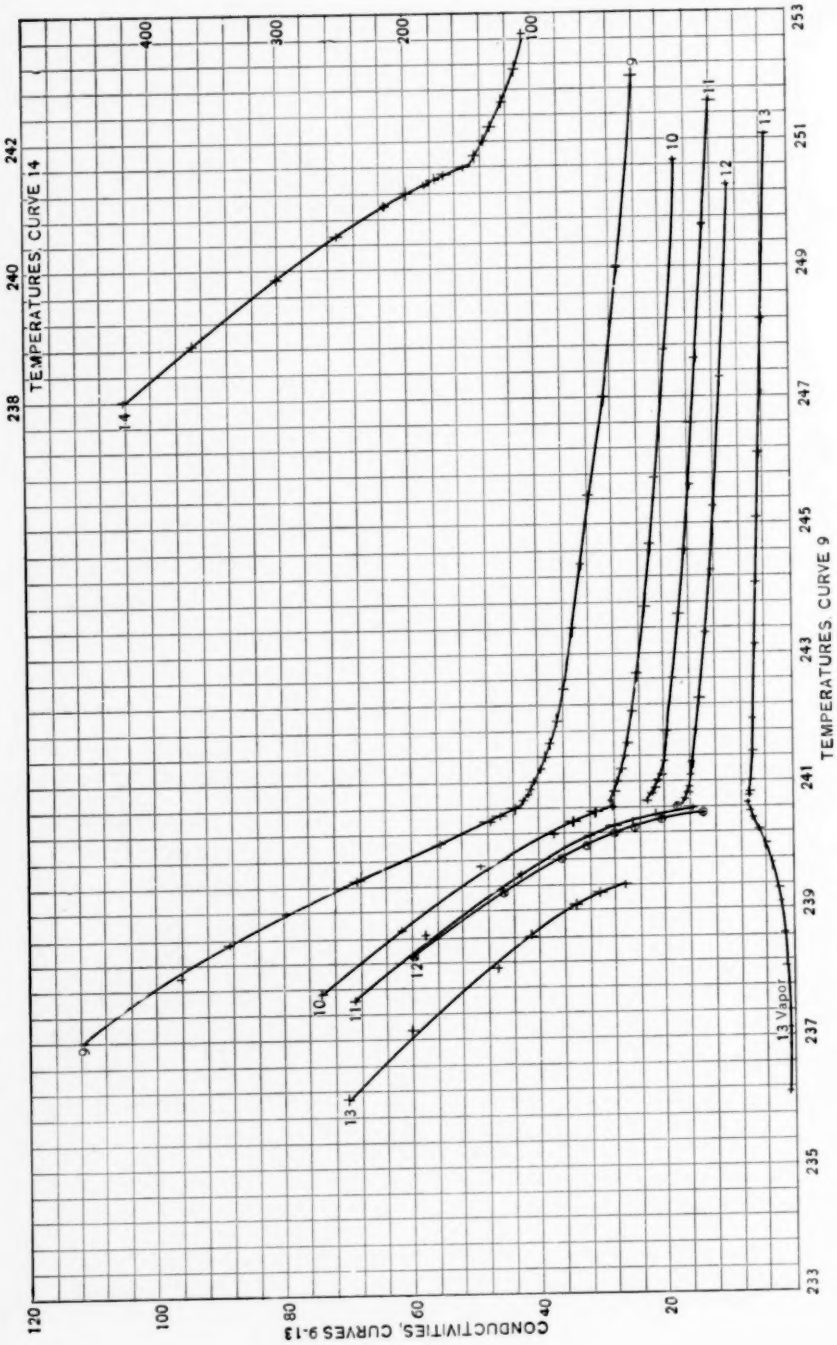
TEMPERATURES, CURVE 14
CONDUCTIVITIES, CURVES 9-13
TEMPERATURES CURVE 9
13 Vapor

Fig. 3.

degree of dissociation is increased. The result is then that the curve as plotted, with the correction as made, will run less steep than it would if the volume and consequently the concentration had been kept constant. It seems necessary then to ascribe the change observed in the tangent to the curve to some intrinsic change in the properties of the liquid taking place at the critical point. In order to test this change further at the critical point, measurements were made on a liquid which was passed through the critical point without stirring. The results obtained in this case are those given in series XIV. and are found plotted in curve 14. The tube employed was constricted at the middle to a very small capillary in order to retard diffusion. Here again a discontinuity takes place in the tangent. No corrections were made for the change in the volume of the solution, for it is probable that the change of the liquidogenous portion of the tube continues beyond the critical point. Even with the constriction there is considerable diffusion as could be readily observed in the decrease of the conductivity, the temperature being kept constant. The result of this in the curve is to make the observed effect at the critical point less pronounced. It is to be borne in mind that the change in the volume at the critical point is very considerable. A tenth of a degree changes the volume by many per cent. In series X., curve 10, Fig. 3., the volume of the solution remained very nearly constant. The curve is in this case noticeably steeper.

To fill a tube with vapor we have merely to choose the amount of liquid such that all the liquid evaporates before the critical point is reached. Series XX., curve 20, gives the results under such conditions. The solution here evaporated 2° before the critical point was reached. No discontinuity is observable, if anything the curve runs straighter than any of the others. In series XIX. the liquid also disappeared a little below the critical point. It is again noticeable that this curve runs somewhat straighter than the curve above it. The same effect is observable in series XIII., curve 13. The liquid here disappeared at 0.2° below the critical point. It is seen then that when the tube is full of liquid at the critical point the curve beyond the critical point is comparatively straight. When the tube is about one half full of liquid at the critical point the

curvature is greatest, and as the quantity of liquid at the critical point decreases the curve again becomes straighter. That the curve beyond the critical point is never quite straight is not surprising. When the tube is full of liquid at the critical point we doubtless

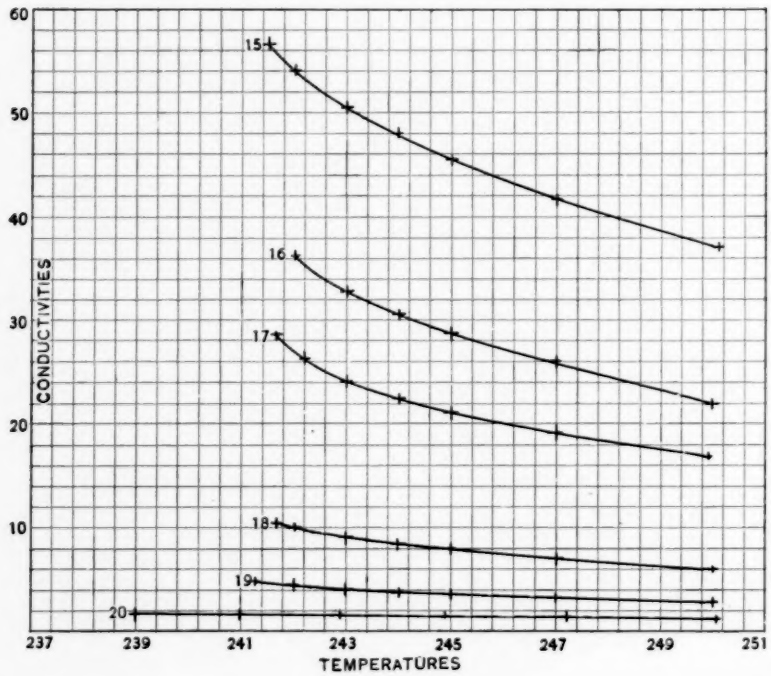

Fig. 4.

have liquidogenous molecules breaking up into gasogenous molecules, while when the tube is filled with vapor the vapor doubtless holds a considerable number of liquidogenous molecules in solution. The breaking up, or possibly the transformation of these liquidogenous molecules into gasogenous ones has as a consequence the curvature of the conductivity-temperature curve. Whether or not the curve ever becomes parallel to the axis of temperatures as Eversheim finds for sulphur dioxide and ammonia[1] is somewhat doubtful.

It rather seems that in the case of the alcohol solutions the curve tends to approach the axis of temperatures asymptotically. In the

[1] Eversheim, Phys. Zs., l. c.

case of the solution which evaporated before the critical point was reached it is certainly very doubtful if there are present enough of the liquidogenous molecules to bring about the observed decrease in the value of the conductivity. It seems more probable that the change is brought about by the decrease in the dissociation of the solute consequent on the change in the molecular forces acting between solute and solvent, upon which the dissociation seems to be dependent. When we take into account the fact that electrolytic dissociation takes place as a rule only in associated liquids, and that the substances dissociated are in general capable of forming definite chemical compounds with the solvent,[1] this contention gains much strength. A case of dissociation in an unassociated liquid could be easily explained on the basis that the dissolved substance may associate itself with the solvent. The same explanation would hold true in explaining the want of dissociation of a dissociable compound in an associated liquid. Thus the acid amides are either very poor conductors or non-conductors when dissolved in water, while they are very good conductors when dissolved in ammonia. The same holds true of some other compounds such as mercuric chloride and mercuric cyanide.[2] These compounds are poor conductors in water, yet in ammonia they are relatively good conductors. At the same time the association has been shown in the case of mercuric chloride in ammonia;[3] it is probable for mercuric cyanide in ammonia. It seems possible therefore that the decrease in conductivity observed for alcohol solutions beyond the critical point is due to a change in the association factor between the solvent and the solute rather than to a breaking up of the liquidogenous molecules into gasogenous ones.

Whether or not a discontinuity of the tangent takes place in the case of non-associated liquids can only be determined by experiment. If it can be shown that such change does not take place, then it will be conclusive evidence that this change in the case of methyl alcohol is due to its association. If, on the other hand, the same change takes place in non-associated liquids, then we must

[1] A. Werner, Zt. f. Anorg. Chem., 3, pp. 294–297, 1893.
[2] Franklin and Kraus, Amer. Chem. Jour., 23, p. 277, 1900.
[3] Franklin and Kraus, l. c., p. 300.

look upon the phenomenon as one characteristic of the change from the liquid to the gaseous state, and our views on the critical phenomenon will have to be modified, since it does not seem possible to account for a discontinuity on the basis of our present views of the critical phenomenon. The curves of Hagenback[1] show a very strong curvature at the critical point which makes it seem probable that the phenomenon in sulphur dioxide is of the same nature as in alcohol.

It is seen that as the critical point is approached the conductivity of the liquid falls below that of the gas just beyond the critical point — curves 10–12, Fig. 3. This is due to the loss of solute

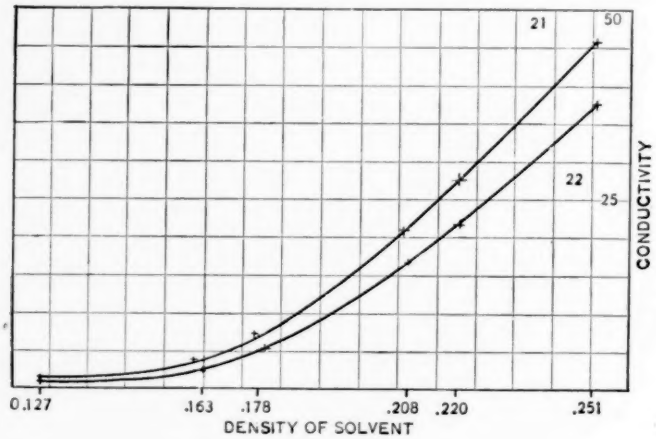

Fig. 5.

by the liquid owing to its greater concentration in the vapor. For this reason it is impossible to follow up the curve at the critical point in any case but that in which the tube is filled with liquid at the critical point. The loss of solute does not become very great except within a few tenths of a degree of the critical point. This will not affect curve 9, for the reason that at the point where the quantity of the solute in the vapor becomes appreciable, the space occupied by the vapor has become very small.

The critical state of a substance affords an excellent opportunity for studying the change of conductivity with varying density of the

[1] A. Hagenback, l. c.

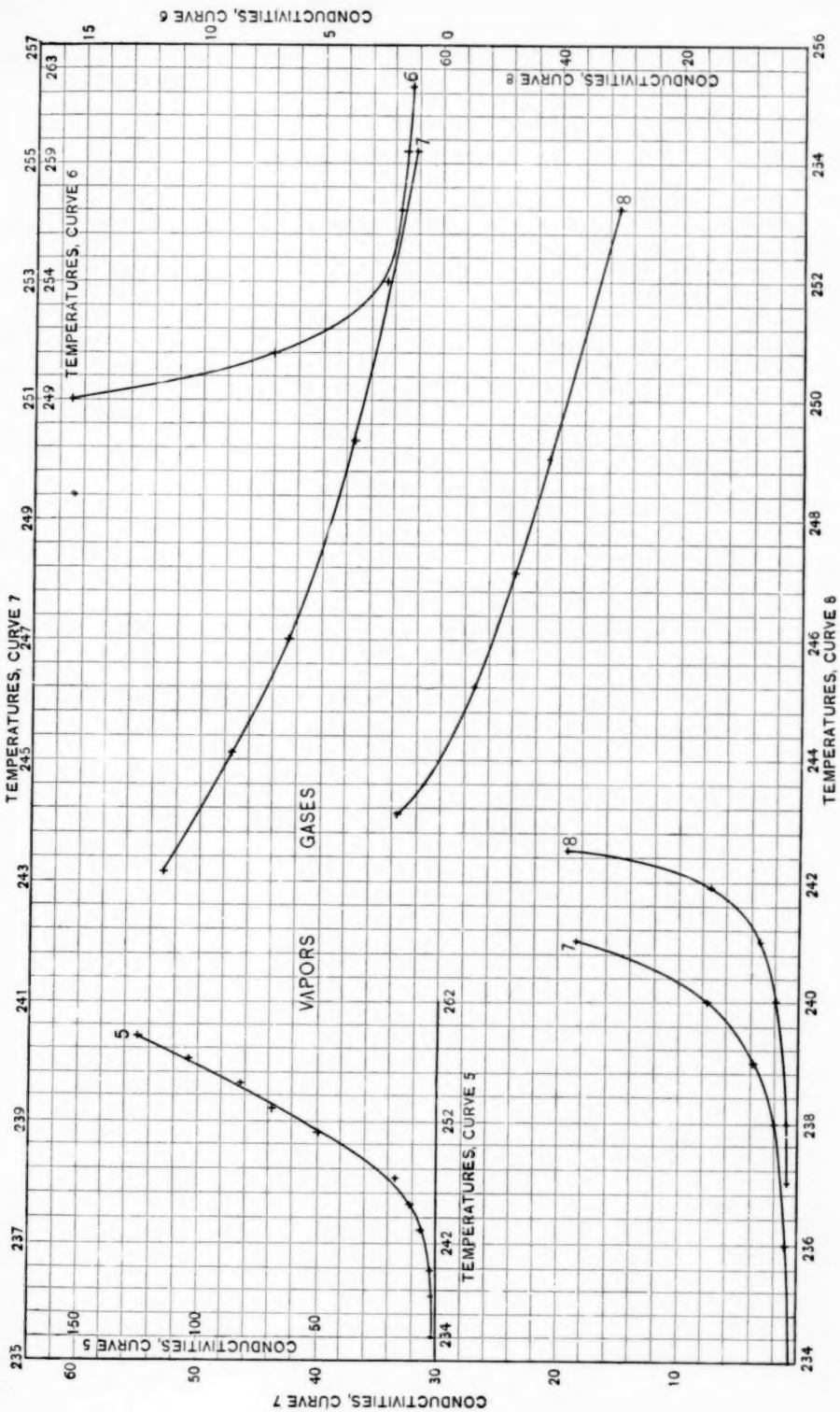
CONDUCTIVITIES, CURVE 6
TEMPERATURES, CURVE 6
CONDUCTIVITIES, CURVE 8
TEMPERATURES, CURVE 7
VAPORS
GASES
CONDUCTIVITIES, CURVE 5
TEMPERATURES, CURVE 5
TEMPERATURES, CURVE 8
CONDUCTIVITIES, CURVE 7

Fig. 6.

solvent. For this purpose the solvent was extracted from the solution as described above, leaving the solute behind. The results are given in series XV.–XX., curves 15–20, Fig. 4. The curves in Fig. 3 were originally intended for the same purpose, but a mishap rendered the concentration of the solvent somewhat inexact, and consequently the curves are useless for this particular purpose. In the case of curves 14–20 the values were obtained for the specific conductivities at 245° and 250°. These values are given in series XXI. and the results are shown graphically in curves 21 and 22 Fig. 5. For larger quantities of solvent the conductivity is very nearly proportional to the quantity of solvent. This would seem to correspond to a solution in which the solvent consists largely of liquidogenous molecules. For smaller quantities of solvent the curve approaches the axis of density of solvent. This would represent the behavior of a gasogenous solution. It is noticeable that the straight line begins to curve at a point corresponding to the density 0.180. It is at this point that the solvent disappeared at the bottom of the tube so that below this point the added solvent was present largely in gasogenous form. The effect due to added solvent becomes much more pronounced as the critical point is approached, as can be seen by comparing the two curves.

The conductivity of vapors possesses some interest. In general the conductivity of a vapor of constant concentration of both solvent and solute decreases with the temperature, as is seen from curve 20. In the case of a saturated vapor, however, the conductivity increases very rapidly as the critical point is approached. This is due to the rapid increase in the concentration of both solvent and solute. A sufficient amount of data has not yet been collected to enable the discussion of the behavior of vapors in detail. A number of curves are, however, given to illustrate their behavior (curves 5–8, Fig. 6). It is probable that curve 20 represents their behavior completely in the case of constant concentration of both solvent and solute.

SUMMARY OF RESULTS.

1. Solutions in methyl and ethyl alcohol possess maxima of electrical conductivity, the former in the neighborhood of 150°, the latter in the neighborhood of 100°.

2. Solutions in methyl and ethyl alcohol conduct beyond the critical point, the former conducting much the better.

3. The temperature coefficient of a solution in methyl alcohol undergoes a sudden change at the critical point. This phenomenon is apparent only when the tube is completely filled with liquid at the critical point, or when the solvent passes through the critical point without stirring.

4. An unsaturated vapor solution exhibits no discontinuity at the critical point of the solvent. Solutions which consist of mixtures of gasogenous and liquidogenous molecules exhibit a great change of the conductivity immediately beyond the critical point, but a discontinuity of the tangent can not be established.

5. Methyl alcohol presents the same phenomena of non-homogeneity beyond the critical point as do other liquids studied in this connection.

6. The conductivity has been studied for solutions possessing the same concentration of solute and different densities of solvent. For large quantities of solvent present the conductivity is nearly proportional to the quantity of solvent. For smaller quantities of solvent present the ratio of increase of conductivity is much smaller. As the critical point is approached, the ratio of increase of conductivity with increase of solvent is increased.

7. The vapor of a solvent may become a very good conductor in the neighborhood of the critical point. The conductivity increases very largely for a saturated vapor as the critical point is approached owing to increasing density of both solvent and solute.

I take great pleasure in acknowledging my indebtedness to Professors Rising and O'Neil, of the Department of Chemistry, for a work room and for the facilities of their department. I wish, moreover, to acknowledge to the other members of the same department my appreciation of the many courtesies extended me.

PHYSICAL AND CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA,
BERKELEY, September, 1903.

SOME EXPERIMENTS ON THE POLARIZATION AND RECOVERY OF CADMIUM CELLS.

BY S. J. BARNETT.

ALL the elements used in these experiments were set up in small H-form vessels by me, following the methods of the Reichsanstalt with unimportant[1] deviations. The cells designated as Nos. 1, 2, and 3 were mounted about the middle of last November, and their e.m.f.s were first compared some ten days later. Their maximum difference was then about 1 part in 10,000, and in recent comparisons (except after severe treatment, described below) they have not differed by more than a few parts in 100,000. Nearly the same degree of excellence, tested either by agreement among themselves or by agreement with the cells of the first group, was attained within a few days after their mounting by Nos. 4, 5, and 6, which were set up on April 13, and Nos. 7, 8, and 9, which were set up on April 16. The mercury used in all the cells was from the same stock, while the other constituents were from different stocks for the cells of the first groups and those set up later. The paste in Nos. 4, 5, and 6 contained no free mercury. The volume of paste in No. 5 and in No. 6 was much greater than in any of the other cells (accounting for their high resistances).

The resistances of the cells were measured by a variety of methods, the only one wholly satisfactory being that of the bridge and secohmmeter with alternating currents. The resistances of Nos. 1, 2, 3, 4, 5, 6, 7, and 9, which will be denoted by B_1, B_2, $\cdots$, B_9, determined by this method on May 12 at 22°.3 C. were $B_1 = 361$, $B_2 = 401$, $B_3 = 342$, $B_4 = 408$, $B_5 = 571$, $B_6 = 587$, $B_7 = 351$, $B_9 = 421$, all in ohms. The resistance at the same temperature of No. 8, obtained by a different method but reduced to correspond with the above values by comparison with other cells whose resistances were determined by both methods, was about 435 ohms.

[1] At least for the purposes of these experiments.

The temperature coefficient of the resistance of the cells at 20° C. was found to be — 0.029. The resistances given above, properly corrected for temperature, were used in calculating the recovery curves given below.

The current through a cell during polarization was read on a Weston millivoltmeter of 5 ohms resistance.

The e.m.f.s of polarization during recovery experiments were determined by the differential method of direct deflections, which offered the advantages of great rapidity and sensitiveness. Two cells, one with normal e.m.f., the other polarized, were connected in series with a galvanometer and a box resistance of 100,000 ohms

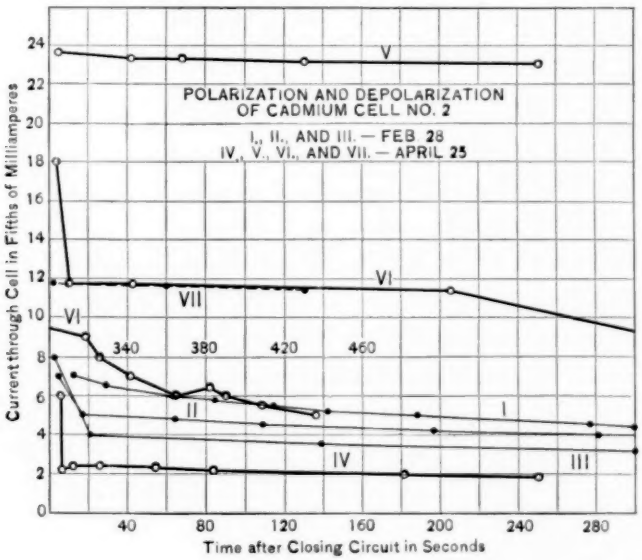

Fig. 1.

and the deflection read. The cells were then opposed to one another in the same circuit, the box resistance plugged out, and the deflection again read. If E_1 and E_2 denote the e.m.f.s of the two cells, B_1 and B_2 their resistances, G the resistance of the galvanometer, and $D+$ and $D-$ the deflections (corrected when necessary) with the cells in series and opposition respectively, the ratio of the difference of the e.m.f.s to their sum is

$$\frac{E_1 - E_2}{E_1 + E_2} = \frac{B_1 + B_2 + G}{B_1 + B_2 + G + 100{,}000} \times \frac{D-}{D+}$$

The method is open to the objection that during the recovery of the cell under test the standard cell is furnishing a current in such a direction as to polarize itself and to hasten the recovery of the other cell. Inasmuch, however, as the current was never greater than about $\frac{1}{1500}$ ampère at its maximum value in the early part of a recovery series, and fell in a few seconds to an excessively small value, the e.m.f of the standard cell was assumed to remain constant in calculating the recovery curves. The same method was used in comparing the e.m.f.s of the cells from time to time, although it must always give somewhat too close an agreement, and was occasionally roughly checked by a potentiometer. In some of the later experiments, in which the e.m.f. of polarization was very great, the box resistance was left in for both deflections.

The galvanometer was a heavy instrument of the Wiedemann type with a highly damped bell magnet, making it possible to begin observations about 6^s after closing the circuit. The variations of the null point were small and easily allowed for. The resistance of the coils used was about 500 ohms.

The time was recorded with a clock and chronograph or with a watch, according to the demands of speed and convenience. The temperature was read when necessary from a thermometer hanging on the wall.

After a few preliminary experiments more accurate observations began on February 28 with No. 1 as standard and No. 2 under test. No. 2 had been frequently short-circuited before, though never for a great length of time.

About $8^h\ 20^m$ $D+$ was 11.5 cm. and $D-$ was inappreciable (0.005 cm. could be detected, though readings were taken in general only to 0.01 cm.). At $8^h\ 22^m$ No. 2 was short-circuited through the millivoltmeter and its deflections and the time were read simultaneously for about five minutes. The observations are platted in Curve I. of Fig. 1.

At $8^h\ 27^m$ the circuit was broken and the cell connected for e.m.f. comparisons (through the galvanometer in opposition to No. 1). Simultaneous galvanometer and time readings were then taken for over ten minutes. From these data and the resistance $B_1 + B_2 + G = 1{,}375$ ohms, the recovery curve was calculated, and is platted as Curve I. of Fig. 2.

After a few resistance experiments the galvanometer was readjusted and $D+$ (= 38.1 cm.) and $D-$ (= 0.20 cm., $E_1 > E_2$ by 0.014 per cent.) were observed. At $9^h\ 32^m$ No. 2 was again short-circuited and a second polarization curve obtained, platted as Curve

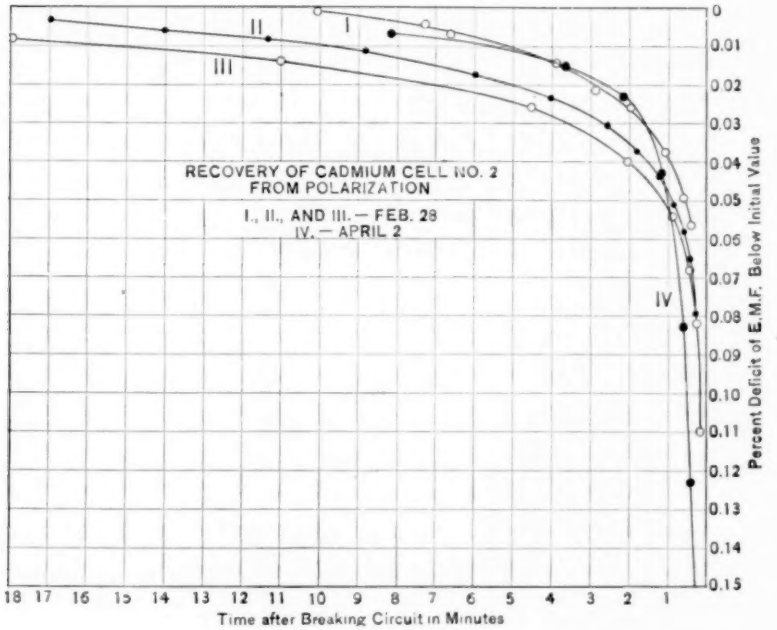

Fig. 2.

II., Fig. 1. After ten minutes the circuit was broken and a series of e.m.f. readings begun. The recovery curve calculated from these observations and from the resistance $B_1 + B_2 + G = 1{,}364$ ohms is platted as Curve II., Fig. 2.

At $10^h\ 44^m$ the cell was again short-circuited, and at $10^h\ 31^m$ the circuit was broken and connections made for e.m.f. comparisons. The polarization observations are platted as Curve III., Fig. 1, and the earlier part of the recovery curve (calculated with $B_1 + B_2 + G = 1{,}353$ ohms) is platted as Curve III., Fig. 2. At $44^m\ 12^s$ after the circuit was broken E_2 differed from its initial value by less than 0.001 per cent. (The initial deflections before the polarization began were $D+ = 38.1$ cm. and $D- = 0.17$ cm., making $E_1 > E_2$ by 0.012 per cent.)

On April 2 several series of experiments were made upon No. 2. The apparatus was so arranged that all the combinations for the different measurements could be made by simply opening or closing keys, inserting plugs, etc.

At $9^h\ 36^m$ No. 2 was short-circuited for 3^m. At $10^h\ 2^m$ the process was repeated. At $10^h\ 39^m$ connections were made for e.m.f. comparisons. $D+$ was found to be 13.2 cm. and $D-$ to be 0.005 cm. ($E_2 > E_1$). At $10^h\ 45^m$ No. 2 was short-circuited through the voltmeter, whose reading fell to 1.7 millivolt at the end of three minutes, when the circuit was broken and the recovery observations began. The galvanometer deflection is platted as a function of the time after breaking the circuit in Curve II., Fig. 4 (the observations being indicated by the circular rings), and the recovery curve is platted in Curve I., Fig. 6. A part of the latter curve is also platted for purposes of comparison in Fig. 2 (Curve IV.). These curves were calculated with $B_1 + B_2 + G = 1{,}373$ ohms.

The low values to which E_2 fell after polarization in these experiments is evident from the polarization data and the fact that the initial current, calculated from the resistances and the initial e.m.f. of the cell, would exceed $1\frac{1}{5}$ milliampère.

To examine the (possible) variation of resistance during the time of recovery the following experiments were performed. An Edison cell (with e.m.f. 0.88 volt on April 3) was connected to the terminals of a resistance box with 1,010 ohms unplugged, and from traveling plugs connected with the terminals of the 10-ohm coil the current was led through the galvanometer, a reversing key, and the two cadmium cells in opposition. When the key was reversed the current was reversed through the cells, but not through the galvanometer. The deflection was read for both directions of the current through the cells, and the mean deflection at any time was taken as inversely proportional to the resistance $B_1 + B_2 + G$. The initial mean deflection was found to be 3.98 cm. No. 2 was then short-circuited for 3^m, at the end of which the circuit was broken and the cells connected as above with the current from the Edison shunt traversing No. 2 in the normal direction ($-$ to $+$). The galvanometer deflections were then observed as a function of the time after breaking the circuit. The results are platted in Curve I., Fig. 3.

After another short-circuit of 3^m, beginning at $12^h\ 3^m$, a similar set of observations was made, but with the current traversing the cells in the opposite direction (+ to − in No. 2). The results are platted in Curve II., Fig. 3.

At 12^h 16–17^m deflections with the current in both directions through the cells were taken, the mean deflections in two sets being 4.00 cm. and 4.02 cm.

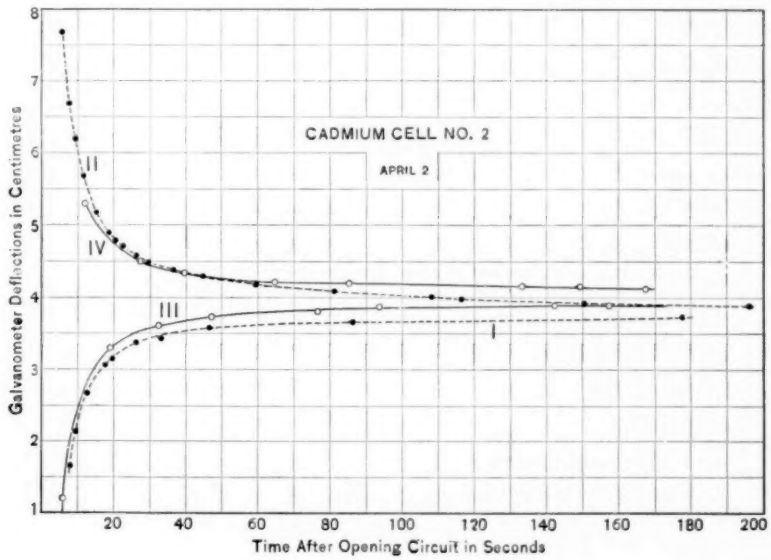

Fig. 3.

With the same connections, No. 2 was short-circuited for 3^m, put on open circuit for 1^m, short-circuited again for 1^m, then put on open circuit at $12^h\ 24^m$ with the current from the Edison shunt traversing it in the normal direction (− to +). The galvanometer deflection was read as soon as the oscillations of the needle had stopped, then the current was reversed through the cells and the deflection read, then reversed again, etc., times being read simultaneously with deflections. The results are platted in Curves III. and IV., Fig. 3; Curve III. containing the results with the current through No. 2 in the normal direction and Curve IV. the results with the current in the opposite direction.

The mean ordinate of Curves III. and IV., Fig. 3, is platted as a

function of the time after open circuit in Curve I., Fig. 4, the first point, however, being obtained from Curves I. and II., Fig. 3.

The black circles on Curve II., Fig. 4, exhibit the relation between the half difference of the ordinates of Curves III. and IV., Fig. 3, and the time, the first point, however, being obtained from Curves I. and II of the same figure.

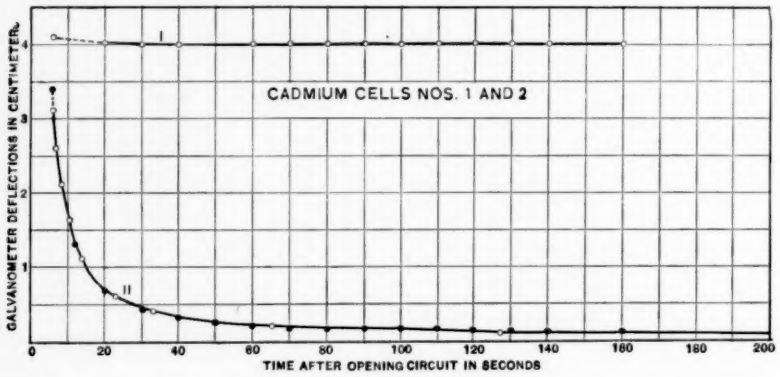

Fig. 4.

The figure (Fig. 4) shows that the resistance of the cells and galvanometer in series did not differ appreciably during the recovery observations from its initial value before short-circuit (deflection 4.01 cm.).

On April 22 observations were made upon cell No. 7, which had not previously been used (except from e.m.f. and resistance comparisons with extremely weak currents). Its initial electromotive force was found to be about 0.002 per cent. greater than that of No. 1.

At $10^h\ 62^m$ No. 7 was short-circuited and its polarization curve obtained. The observations are platted in Curve I., Fig. 5.

At $11^h\ 22^m$ the circuit was broken and recovery observations began. The results are platted in Fig. 6, Curve III., calculated with $B_1 + B_7 + G = 1{,}248$ ohms.

No. 7 was short-circuited again at $11^h\ 59^m$, and once more at $12^h\ 15^m$. The two sets of polarization observations are platted in Curves II. and III., Fig. 5.

The occurrence of maxima in some of the polarization curves is not peculiar to No. 7.[1] Such maxima have been observed with No.

[1] Nor is it peculiar to cadmium cells. Nov. 14, 1903.

2 (as in Fig. 1, Curve IV.) and with No. 3, and would doubtless occur with any of the others if short-circuited sufficiently, unless perhaps the resistance of some of the cells is too great. In such cases maxima of the same kind could doubtless be produced by increasing the polarization current with the aid of an additional e.m.f., as in the case of Curve VI., Fig. 1 (see below).

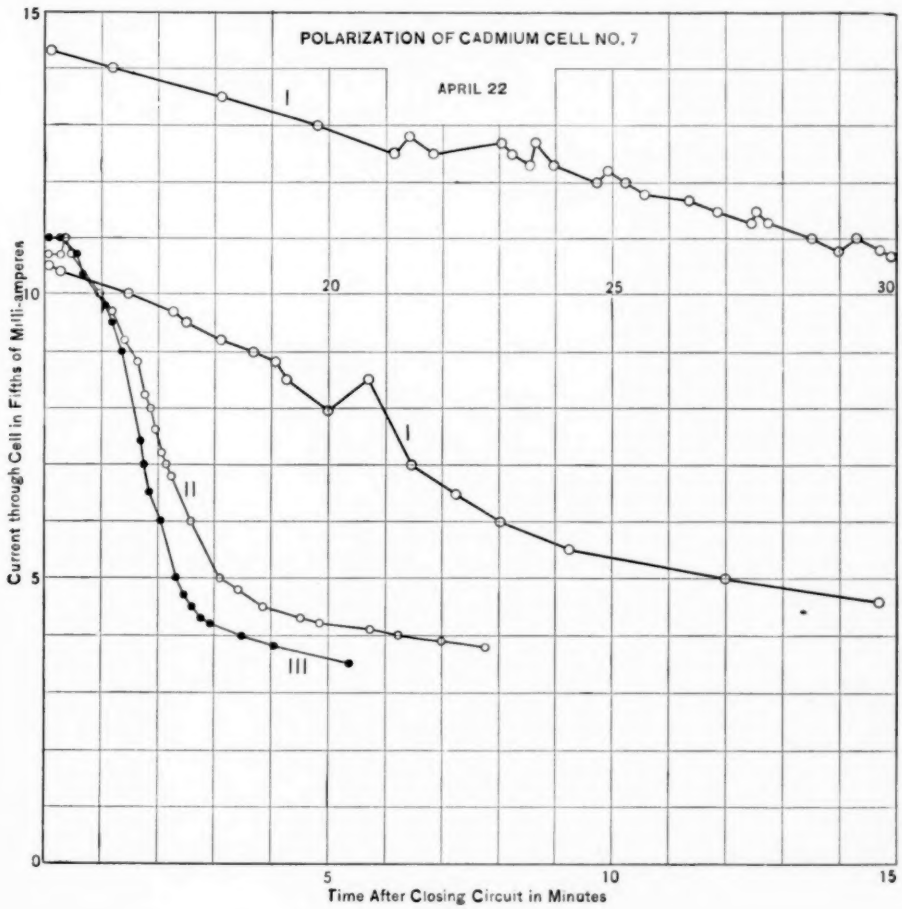

Fig. 5.

On April 25 cell No. 7, whose e.m.f. was then initially about 0.006 per cent. greater than that of No. 1, was short-circuited (without the voltmeter) at $8^h\ 41^m$, and was so left until $12^h\ 52^m$, when the circuit was broken. At $12^h\ 53^m$ the e.m.f. of No. 7 was

only 9.7 per cent. of its normal value. Two days later its e.m.f. was less than that of No. 1 by only 0.001 per cent.

On April 25 some experiments were also performed upon Nos. 6 and 9, which had not been previously short-circuited. The initial differences between their e.m.f.s and that of No. 5, with which they were compared throughout the experiments, were 0.002 per cent. and 0.003 per cent.

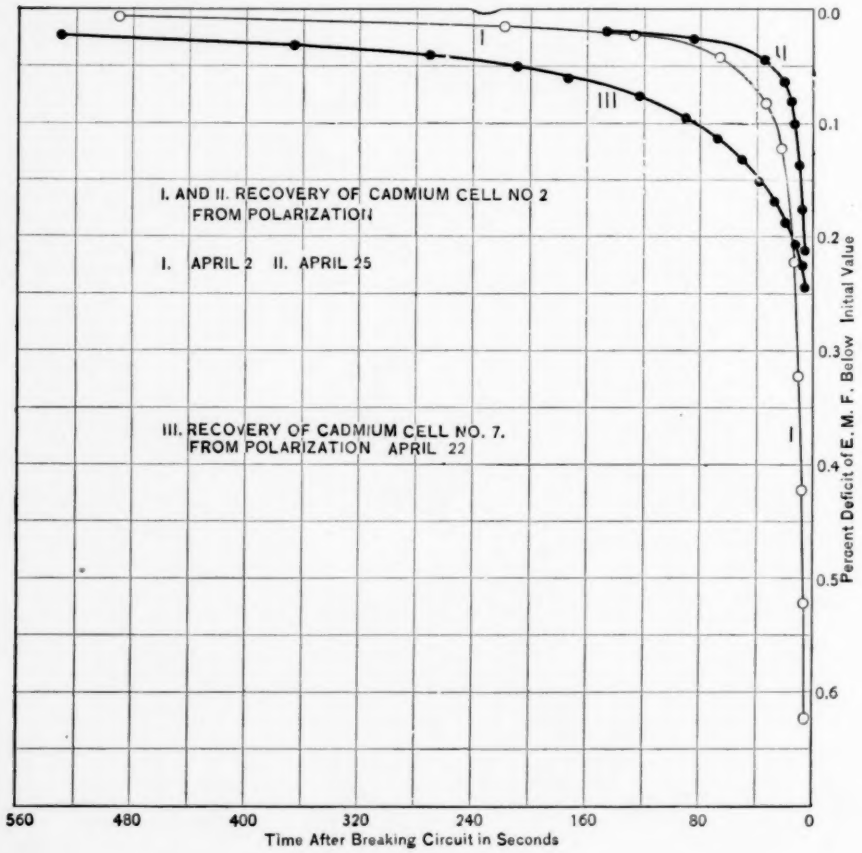

Fig. 6.

The polarization observations upon No. 9 are platted in Curve I., Fig. 7. Seven and one half minutes after the circuit was broken the e.m.f. had risen to within 0.02 per cent. of its initial value.

Cell No. 6 was short-circuited on the same day at $11^h\ 48^m$ and the circuit broken at $11^h\ 56^m$. The polarization observations are

platted in Curve II., Fig. 7. Four minutes after breaking the circuit the e.m.f. had recovered to within 0.03 per cent. of its initial value. At $12^h\ 0^m$ No. 6 was again short-circuited. The polarization observations are platted in Curve III., Fig. 7. In 16^m after opening the circuit the e.m.f. had risen to within 0.1 per cent. of its original value.

On the same day (April 25) some experiments were also made upon No. 2, whose e.m.f. was initially 0.0037 per cent. greater than that of No. 1. At $9^h\ 50^m$ No. 2 was short-circuited. The polarization observations are platted in Curve IV., Fig. 1. Although the cell had not been short-circuited since April 2, the curve shows all the peculiarities of an experienced cell.

About 4^m later the circuit was broken and recovery observations began. The results (calculated with $B_1 + B_2 + G = 1{,}378$ ohms) are platted in Curve II., Fig. 6.

A single chloride accumulator (e.m.f. = 2.03 volts) was then arranged to be connected through a key to the terminals of No. 2, with its positive pole to the negative pole of No. 2. The key was closed at $10^h\ 11^m$ and opened at $10^h\ 15^m\ 9^s$. The observations are platted in Curve V., Fig. 1. After open circuit connections were made for e.m.f. comparisons (with 100,000 ohms in the circuit for both arrangements of the cells). At $10^h\ 22^m$ and $10^h\ 38^m$ the e.m.f. of No. 2 was 7.3 per cent. and 9.4 per cent., respectively, of its initial value.

The same accumulator was then closed in the opposite direction through No. 2 (at $10^h\ 40^m$), and Curve VI., Fig. 1, was obtained. The circuit was broken at $10^h\ 48^m$. Two minutes later the e.m.f. of No. 2, which had increased greatly after 200^s charging, was found to exceed that of No. 1 by only 0.1 per cent., which was reduced in 7^m more to 0.04 per cent.

In the first case (Curve V.) E_2 was reduced almost to zero, and in the second case (Curve VI.) it recovered its normal value within a few seconds. The resistance of the circuit did not alter greatly, if at all, at least in the earlier parts of the experiments.

The accumulator was then again connected to No. 2 (in opposition) and so left for 5^m. Two minutes after breaking the circuit ($11^h\ 3^m\ 25^s$) its e.m.f. was only 0.17 per cent. greater than that of No. 1. At $12^h\ 44^m$ the excess was only 0.02 per cent.

At $12^h\ 46^m$ No. 2 was short-circuited through the voltmeter. The observations are platted in Curve VII., Fig. 1, which resembles closely the polarization curve of a fresh cell. The approximate coincidence between this curve and a part of Curve VI. is due to the fact that the e.m.f. of the accumulator was almost exactly twice that of the cadmium cell. The e.m.f. of No. 2, on being tested just after breaking the circuit, was found to *exceed* that of No. 1 by 0.06 per cent. — a greater difference than before. Two days later the excess was 0.016 per cent.

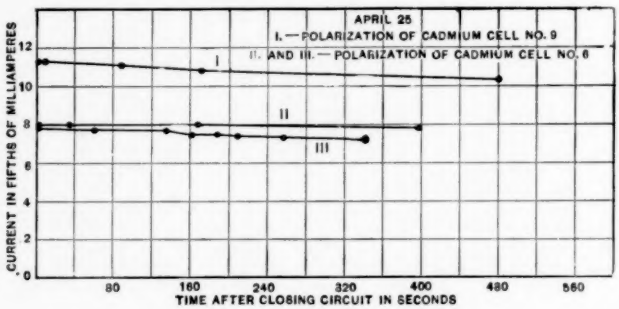

Fig. 7.

At $11^h\ 10^m$ two accumulators in series (e.m.f. = 4.1 volts) were connected to the terminals of Nos. 4 and 8 in opposition with the current in the normal direction through No. 8, and were so left until $12^h\ 26^m$, when the circuit was broken. At $12^h\ 31^m$ the e.m.f. of No. 8 was only 6.9 per cent. of its original value, while that of No. 4 exceeded its initial value by 4.7 per cent. Two days later No. 8 had recovered to within about 0.006 per cent. of its normal e.m.f. and No. 4 to within about 0.09 per cent.

On May 2 at $12^h\ 52^m$ a dynamo with an e.m.f. of about 93 volts was connected in series with No. 4 and No. 8 in opposition, the current traversing No. 4 in the normal direction. Ten minutes later the cells had become considerably heated, and the upper part of the mercurous sulphate and adjacent liquid in No. 8 greatly perturbed. The circuit was then broken, and closed again a little later. At the end of about 2^m No. 8 exploded and broke the circuit. The e.m.f. of No. 4 was then tested and found to have fallen to 5.5 per cent. of its original value. On May 2 it had risen

to 6.0 per cent., on May 7 to 9.4 per cent., and on May 12 to within about 0.27 per cent. of its initial value. Shortly after the last comparison the cell was charged for 1^m with a single accumulator (through the millivoltmeter). The e.m.f. was then found to exceed E_1 by 0.3 per cent., the excess rapidly diminishing to 0.15 per cent. On May 15, E_1 exceeded E_4 by 0.04 per cent.[1] (On May 12 the resistances of all the cells had been measured, both by alternating currents and by a charging current from 2 accumulators.)

Also on May 2, about 1^h 10^m, the dynamo was connected in opposition to No. 7 and so left for about 30^s. The e.m.f., on being tested quickly after opening the circuit was found to exceed E_1 by 0.054 per cent., the excess decreasing to 0.04 per cent. by the next morning. On May 7 the e.m.f. of No. 7 was greater than that of No. 1 by 0.024 per cent. and on May 12 by 0.01 per cent. On May 15 the e.m.f. of No. 1 exceeded that of No. 7 by 0.001 per cent.

In most of the experiments here described I have been assisted by one of my students, Mr. C. K. Studley.

STANFORD UNIVERSITY, CALIFORNIA,
May 16, 1903.

[1] In a comparison made yesterday E_1 exceeded E_4 by only about 0.004 per cent. Nov. 14, 1903.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE TWENTY-SECOND MEETING.

THE annual meeting of the Physical Society was held at the Central High School, St. Louis, Mo., on Wednesday, December 30, 1903, in coöperation with Section B of the American Association for the Advancement of Science.

Tellers being appointed by the President, the ballots for the annual election were counted and the following named officers were elected: President, Arthur G. Webster; Vice-President, Elihu Thomson; Secretary, Ernest Merritt; Treasurer, William Hallock; Members of the Council, E. Rutherford and W. S. Franklin.

The report of the treasurer for the year 1903 was read by the secretary. The report is printed below.

The following papers were presented:

1. The Radioactivity of Ordinary Metals. E. F. BURTON.

2. Does the Radioactivity of Radium Depend upon the Concentration? E. RUTHERFORD.

3. The Heating Effects of the Radium Emanation. E. RUTHERFORD and H. T. BARNES.

4. The Phosphorescence of Organic Substances at Low Temperatures. Preliminary Note. E. L. NICHOLS and ERNEST MERRITT.

5. The Spectro-photometric Study of Fluorescence. E. L. NICHOLS and ERNEST MERRITT.

6. On the Electrical Conductivity of Liquid Films. LYMAN J. BRIGGS.

7. On the Use of Nickel in the Core of the Marconi Magnetic Detector. ARTHUR L. FOLEY.

8. On Double Refraction in Matter Moving through the Ether. D. B. BRACE.

9. Electric Double Refraction in Gases. D. B. BRACE.

10. The Work of the National Bureau of Standards. E. B. ROSA.

11. The Spectrum of the Afterglow of the Spark Discharge in Nitrogen at Low Pressures. PERCIVAL LEWIS.

12. The Spectrum of the Electrodeless Discharge in Nitrogen. PERCIVAL LEWIS.

On behalf of the Council the secretary made the following announcements:

Accepting an invitation from the Philosophical Society of Washington, the Council has decided to hold the spring meeting of the Physical Society in the year 1904 in Washington. The date of the meeting is to be decided by the officers of the Physical Society and will be announced later.

The Physical Society has been invited by the Committee of Organization of the International Electrical Congress to hold a meeting in St. Louis, in connection with the meeting of the Congress, during the month of September, 1904. The Council voted to accept this invitation, provided that mutually satisfactory arrangements could be made. It is the sense of the Council that a definite plan should be presented by the Council at this meeting for the establishment of a western section of the Physical Society.

ERNEST MERRITT,
Secretary.

Adjourned.

TREASURER'S REPORT FOR 1903.

Receipts.		
Balance from 1902	$1406.49	
Interest on the same to Dec. 31, 1903	49.23	
Arrears of dues for previous years	150.00	
Three life membership fees	150.00	
Annual dues	930.00	
Total		$2685.72
Disbursements.		
Printing, Andrus and Church	$ 102.40	
Subscriptions to Physical Review	591.00	
Subscriptions to Science Abstracts	295.50	
Office of the Secretary	112.34	
Office of the Treasurer	27.37	
Total		$1128.61
Balance carried forward		1557.11
Total		$2685.72

WILLIAM HALLOCK,
Treasurer.

DOES THE RADIOACTIVITY OF RADIUM DEPEND UPON ITS CONCENTRATION?[1]

BY E. RUTHERFORD.

BY the electric method, the intensity of the γ radiation from a known quantity of radium, in a state of radioactive equilibrium, was determined first in the form of pure solid radium bromide and second

[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

when dissolved in a solution of radium chloride of more than a thousand times the volume of the solid radium bromide. No appreciable difference in the intensity of the γ rays was observed in the two cases, although the experiments were continued over a month's interval. Since the intensity of the γ rays serves as a comparative measure of the radioactivity of radium, it may be concluded that, over the range examined, the radioactivity of radium is independent of its concentration. This result shows that the rate of disintegration of radium and its products is not appreciably altered by the bombardment of its own powerful radiations, and renders it probable that the radioactivity of radium is, in all cases, directly proportional to the amount of that element present.

HEATING EFFECT OF THE RADIUM EMANATION.

BY E. RUTHERFORD AND H. T. BARNES.[1]

AN account of some preliminary experiments to show that the radium emanation, together with the secondary products which arise from it, was responsible for a large proportion of the heat emission of radium was given in *Nature* (October 29, 1903). Further results on this question were communicated to the Physical Society. The emanation from thirty milligrams of pure radium bromide was released by heat and condensed in a small glass tube immersed in liquid air. The variation with time of the heating effect of the deëmanated radium and of the tube containing the emanation was determined at regular intervals for over a month. A special form of differential air calorimeter was employed to measure the small heating effect involved. It was found that the heating effect of the emanation tube increased to a maximum after about three hours, and then decayed according to an exponential law with the time, falling to half value in a little less than four days. The heating effect of the deëmanated radium fell rapidly in the course of three hours to a minimum, corresponding to 25 per cent. of its original value and then slowly increased again with the time, recovering its original value after an interval of about one month. At any time during the whole course of the experiment the sum total of the heating effect of the deëmanated radium together with that of the emanation tube was constant and equal to that of the original radium. At any time t after reaching its maximum, the rate of heat emission Q_t of the emanation tube was given by $Q_t/Q_0 = e^{-\lambda t}$ where Q_0 is the maximum rate and $\lambda = .0077$ when an hour is taken as the unit of time. The rate of heat emission Q_t of the radium at any time t after reaching the minimum is

[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

given by $Q_t/Q_0 = .25 + .75(1 - e^{-\lambda t})$ where Q_0 is the maximum rate and λ the same constant as before.

The variation of the heating effects with time, expressed by the above equations, is exactly the same as the variation of the radioactivity of the emanation and of the radium from which it has been separated, *measured by the α rays.*

The rapid initial changes of the rate of heat emission of radium after removal of the emanation and of the emanation tube after the introduction of the emanation were determined by means of a pair of differential platinum thermometers wound on the inside surface of a glass tube. By this method, observations could be made with more rapidity and certainty than by the air calorimeter. It was found that the heating effect of radium had fallen to about 59% of its original value 10 minutes after removal of the emanation. It then diminished steadily to a minimum of 25% after the lapse of 2 to 3 hours. After the heating effect of the emanation tube had risen to a maximum, the emanation was withdrawn and the diminution with time of the heating effect determined. There was a rapid drop during the first 10 minutes to about 45% of the maximum, then a slower change, and finally a more rapid decrease to zero according to an exponential law, falling to half-value in 30 minutes.

The curves showing the rise of the heating effect of the emanation to a maximum, and of the diminution of the heating effect of the emanation tube to zero after removal of the emanation, were found to be complementary to one another. The rapid fall and rise of the heating effect of the deëmanated radium and of the emanation tube respectively are connected with the fall and rise respectively of the "excited activity" produced by the emanation. It was suggested that the name emanation X be given to the matter which causes "excited activity" on bodies. On this view, the radium changes into the emanation and the emanation into emanation X. There are three further changes in the matter called emanation X. In the first change half the matter is transformed in 3 minutes, in the second change half in 34 minutes, in the third change half in 28 minutes. On account of the first rapid initial change in emanation X, it has not yet been found possible to separate the heating effect of the emanation from that due to the first change.

The results obtained are shown in the following table.

Active Products.	Nature of Rays.	Percentage Proportion of Activity Measured by the α Rays.		Percentage Proportion of Total Heating Effect.
Radium (freed from active products).	α rays.	25		25
Emanation.	α rays.	18	34	41
Emanation X (first change).	α rays.	16		
" (second change).	No α rays.	0	42	34
" (third change).	α β and γ rays.	42		

The results, as a whole show, that the heat emission of radium is an accompaniment of the expulsion of α particles and that the time-variation of the heating effect of each of the different active products is the same as the time-variation of the activity measured by the α rays. The heat emission of radium is probably due in part to the kinetic energy of the expelled α particles and in part to the energy released consequent upon the rearrangement of the components of the systems left behind after the expulsion of the α particle.

It was deduced that the emanation, released from 1 gram of radium, gave out an amount of heat during its life corresponding to about 10,000 gram calories. It has been shown (Rutherford, *Nature*, Aug. 20, 1903) that the volume of the emanation released from 1 gram of radium probably lies between 6×10^{-4} c.c. and 6×10^{-5} c.c. at standard pressure and temperature. Assuming the density of the emanation to be about 100 times that of hydrogen, 1 gram of the emanation would during its life radiate an amount of energy lying between 2×10^{9} and 2×10^{10} gram calories. One-pound weight of the emanation would initially radiate energy at the rate of 10^{4} to 10^{5} H. P. and would emit during its life an amount of energy between 6×10^{4} and 6×10^{5} horsepower-days.

There can thus be no doubt that matter, under special conditions, is capable of emitting an amount of energy enormous compared with that released in the most intense chemical reactions. On the disintegration hypothesis (Rutherford and Soddy, *Phil. Mag.*, May, 1903) this energy is derived from the energy latent in the radium atoms and is released during the successive stages of their disintegration.

THE PHOSPHORESCENCE OF ORGANIC SUBSTANCES AT LOW TEMPERATURES, PRELIMINARY NOTE.[1]

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

THE experiments here described are preliminary to a more extended study of phosphorescence and fluorescence at low temperatures, which will be, as far as possible, quantitative in character. Before undertaking quantitative experiments it seemed advisable, however, to test a large number of substances qualitatively, so as to determine which are best suited for further study.

The substances thus far tested are chiefly organic compounds of definite composition. Although a few had already been tried by Dewar, most of the substances had not been previously tested. Of the 120 substances tested only 21 failed to show either phosphorescence or fluorescence, or both, when cooled to the temperature of liquid air.

[1] Abstract of apaper presented at the meeting of the Physical Society held on December 30, 1903.

The method of testing was briefly as follows: The substance was placed in a glass or porcelain dish in a dark room, and covered with liquid air, which was poured directly upon it. It was then illuminated by the light from a spark passing between magnesium terminals. Fluorescence, if at all intense, could be at once detected; while phosphorescence, if present, was observed after the spark had been stopped. By causing the light to pass through glass before reaching the specimen it was easy to determine whether the effects were caused by the ultra-violet or the visible rays. Each substance was also tested at ordinary temperatures. In the case of about one hundred substances the effect of X-rays was also tried, both at ordinary temperatures and when the substances were cooled by liquid air.

Previous experiments have shown that, as regards the effect of low temperatures on phosphorescence, bodies may be divided into at least three classes (1) substances in which the power to phosphoresce is increased by cooling; (2) substances which are phosphorescent at ordinary temperatures, but which have this power diminished or destroyed at low temperatures; (3) bodies whose behavior, as regards phosphorescence, is apparently unaffected by cold.

We have found many examples of the first class and some examples of the third; but among the organic substances studied no example of the second class was found. Balmain's paint and the phosphorescent sulphides are the only substances tested by us which show diminished phosphorescing power when cooled.

The effect of cold is manifested in a great variety of ways. Certain substances which show no luminescence at ordinary temperatures remain unaltered. Others, which are phosphorescent at ordinary temperatures, become more intensly so when cooled in liquid air. Phthalic acid and isophthalic acid are good illustrations of this class. Other substances, which are not luminescent at ordinary temperatures, become brilliantly so when cooled. Anthraquinone, ethyl carbamate, palmitic acid, and cetyl alcohol show intense phosphorescence at low temperatures, but none at all at 18°C. Certain substances, such as oxalic acid and piperine, develope the power of fluorescing at low temperatures. And, finally, there are many substances which become both phosphorescent and fluorescent when cooled in liquid air. Tetra-chlor-phthalic acid is a good example. This substance is also remarkable for the brilliant fluorescence produced, at low temperatures only, by the X-rays.

The X-rays seem much less effective in producing luminescence at low temperatures than light. In the case of tetra-chlor-phthalic acid the fluorescence is as brilliant as that of an ordinary X-ray screen. In several other cases also fairly intense phosphorescence or fluorescence is produced. But the greater number of the substances tested failed to respond.

In several instances there are indications that substances which are closely related chemically behave in a similar manner as regards their luminescence. The case of benzoic acid and calcium benzoate is perhaps the most striking. The various modifications of phthalic acid also show a general resemblance in their behavior. On the other hand, instances are far more numerous in which the chemical composition would lead us to expect similar behavior, while in reality none is observed. It has therefore been impossible, thus far, to develop any law connecting luminescence with chemical composition.

THE SPECTRO-PHOTOMETRIC STUDY OF FLUORESCENCE.[1]

BY E. L. NICHOLS AND E. MERRITT.

THE law expressed by Stokes in his memoir entitled "Change of Refrangibility of Light," Philosophical Transactions, page 463, 1852, to the effect that in fluorescence the wave-length of the fluorescent spectrum is always greater than that of the exciting light has been called in question by Lommel[2] who pointed out that for certain fluorescent bodies there is an unmistakable overlapping of the regions in the spectrum occupied by the exciting waves and by the fluorescent light produced. Lommel drew the further conclusion that for this class of fluorescent substances the character and composition of fluorescence was independent of the wave-length of the exciting source. Lommel's exception to Stokes' law has found confirmation at the hands of Hagenbach, Stenger and others but his conclusions have been rejected and the universal accuracy of Stokes' law reaffirmed by Lamansky, Becquerel and others. It is the purpose of this paper to apply to the solution of this still open question the methods of the spectrophotometer. The authors have succeeded in getting data from which curves showing the distribution of intensities in the spectrum of fluorescene and of other substances, belonging to the same class can be plotted.

The most important conclusions reached in this paper are as follows:

(1) Not only in the case of these substances is Stokes' law inapplicable, but fluorescence can be excited by light, the wave-length of which is greater than that of the maximum of the fluorescent spectrum.

(2) Lommel's statement with reference to the independence of the fluorescent spectrum of this class of substances from the character of the exciting source is fully justified. The curves for fluorescence when excited by white light, by nearly monochromatic light of mean wave-length

[1] Abstract of a paper presented at the meeting of the American Physical Society held on December 30, 1903.

[2] Lommel, Poggendorff's Annalen, 143, 159 and 160; also Wiedemann's Annalen, 8 and 30.

.5246, wave-length .494, and wave-length .465 gave curves identical as regards the position of the maximum, which in all cases was located at wave-length .517 μ. The shape of these curves is such as to indicate complete independence between the character of the exciting source and that of the fluorescence produced.

Electrical Conductivity of Liquid Films.[1]

By L. J. Briggs and J. W. McLane.

Reinold and Rücker[2] have found that the specific conductivity of a hard soap film increases as the thickness of the film decreases. In the case of Plateau's solution (*liquide glycerique*) no change in the specific conductivity of the film was observed down to a thickness of 374 $\mu\mu$. These conclusions are based upon the measurement of the thickness of the film by an optical method, which involves the assumption that the index of refraction of the film is the same as that of the solution in mass.

The writers have recently made some preliminary measurements of the specific electrical conductivity of films of Plateau's solution by another method, in which the thickness of the film is calculated from the surface area and *weight* of the film.

The measurements were made on a cylindrical film supported horizontally on two parallel platinum rings. The rings were soldered to two parallel vertical copper wires, which were held in a small ebonite frame. The film was enclosed during the measurements in a double-walled vessel, the walls of the inner vessel being kept moistened with the soap solution. The upper part of the frame passed through a slit in the cover of the vessel, and could be attached to the balance or to the bridge as desired.

Preliminary measurements by this method show that the specific electrical conductivity of a film approximately 1 μ in thickness is less than *one third* that of the solution in mass. The method involves the assumption that the density of the film is the same as that of the liquid in mass.

Bureau of Soils, Washington, D. C.,
December 24, 1903.

[1] Abstract of a paper presented at the meeting of the Physical Society held on December 30, 1903.

[2] Phil. Trans., 1883, part 2, p. 645; 1893A, p. 505.

THE SPECTRUM OF THE ELECTRODELESS DISCHARGE IN NITROGEN.[1]

BY PERCIVAL LEWIS.

SOME general observations of the spectrum of the electrodeless discharge in various gases, and in gaseous mixtures showing an afterglow, have been made by J. J. Thomson[2] and by Newall,[3] but no systematic work seems to have been done on such spectra. The fact that in the ring discharge there is no passage of electricity between electrodes and the gas, no finite discontinuities nor even a potential gradient in the path of the current, and that the pressure in the gas is much less than that ordinarily employed in vacuum tubes, render it possible that some characteristic peculiarities may be observed in such spectra.

Nitrogen is a particularly interesting subject to study in this connection, as it has such a multiplicity of spectra, and several groups of bands which behave quite differently under given conditions. As it is often assumed that the negative-pole spectrum is due to cathode rays, it is also of interest to see whether the negative-pole bands appear in the spectrum of a discharge where there is no cathode.

The writer has recently obtained some preliminary results. The nitrogen was prepared by heating a solution of sodium nitrite and ammonium sulphate, mixed in molecular proportions. It was freed from traces of oxygen by bubbling through an alkaline solution of pyrogallic acid, and from carbon dioxide and water vapor by passing it through a concentrated solution of caustic potash and drying tubes.

The discharge tube was a spherical glass bulb, provided with a quartz window. Around it was a pasteboard cylinder on which were wound eight turns of heavy wire in circuit with a spark gap and condenser. The pasteboard cylinder was moistened to screen the tube from electrostatic effects, and the helix usually connected to earth. The ring was always very clearly defined, indicating that the electrostatic effects were at least very small.

At first the discharge was a coppery pink, characteristic of pure nitrogen. After a time it turned white, as likewise observed by J. J. Thomson, but the spectroscope showed without a doubt that the whiteness was due to mercury vapor from the pump, not to nitrogen, nor even to carbon compounds, the spectrum of which was vanishingly weak. Photographs were taken with a small quartz spectrograph, giving spectra of about 4 inches in length from λ 5,800 to λ 2,100.

[1] Abstract of a paper presented to the Physical Society on December 30, 1903.

[2] Thomson, Phil. Mag., 32, 1892.

[3] Newall, Proc. Camb. Soc., 9, p. 295, 1897.

Deslandres[1] showed that in the spectrum of the positive column in nitrogen there are three distinct groups of bands, which are differently affected by physical conditions. The first group comprises most of the visible spectrum, and is attributed by Deslandes to pure nitrogen. The second begins in the violet and extends to about λ 2,800, and is supposed by him to be due to nitrogen and hydrogen. The third begins at about λ 3,000 and extends to λ 2,100. This group he considers dependent on the presence of traces of oxygen, as metallic sodium heated in the tube will eliminate it.

In the photographed spectrum of the ring discharge the third group is either entirely lacking, or with the longest exposures only faint traces of the strongest bands are visible. The second group of bands is strong. The first group is fairly strong. The difference between this spectrum and that of the simple induction discharge between electrodes is clearly shown by comparison with a plate showing the latter.

It is perhaps even more interesting to note that the negative bands also appear on all the plates, although weak in comparison with the positive bands. The only apparent way to reconcile this with the view that the negative bands are due solely to cathode rays seems to be to assume that there are electrostatic discharges from the glass walls, which thus act as electrodes. Some believe that the spectrum at the negative pole is due to the higher temperature at the cathode. It is very easy, however, to evoke the negative glow by merely placing the finger on the bulb, and no very high temperature seems possible with such a discharge. Whether or not the negative pole spectrum is due to cathode rays, it seems certain that it is not due to any temperature differences.

The stronger mercury lines, as well as some other lines not yet identified, appear on all the plates, as well as the strongest bands due to water vapor.

The Spectrum of the Afterglow of the Spark Discharge in Nitrogen at Low Pressures.[2]

By Percival Lewis.

THE afterglow or phosphorescence often observed in vacuum tubes under certain conditions has been studied by many investigators.[3] In most of these cases, except that where pure oxygen is used (J. J. Thomson and Newall) the phosphorescence was observed in gaseous mixtures,

[1] Deslandres, Ann. Chim. Phys. (6) 15, p. 46, 1888.

[2] Abstract of a paper presented to the Physical Society on December 30, 1903.

[3] See Kayser, Lehrbuch der Spectroscopie, Vol. 1, p. 249; Newall, Proc. Camb. Soc., 9, p. 295, 1897.

it was produced by the simple induction or electrodeless discharge, and the spectrum was continuous — except possibly in one case where Thomson observed lines or bands with the ring discharge where nitrogen was used, and in the case of the afterglow arising from change of pressure in oxygen (Newall).

In 1899 the writer observed an afterglow which seemed different from those previously observed, both in origin and spectrum.[1] It was produced in nitrogen as pure as could be readily obtained, not in mixtures; it was produced only by a powerful discharge with spark gap and condenser, not at all by the simple induction or ring discharge; its visible spectrum was not continuous, but consisted of narrow bands or diffuse lines. The wave-lengths of these lines were difficult to determine accurately, but were about λ 6240, 5780, 5740 and 5410. The afterglow consisted of a rich chamois yellow fog, extending several inches into the connecting tubes. It persisted for several seconds after the discharge had ceased. It quivered and pulsated, and when fresh nitrogen was admitted the glow was driven as a luminous cloud before it, as in a similar case observed by Warburg.[2] It occurred through a wide range of pressures, ranging from a few millimeters to as high a pressure as would permit the passage of the discharge. The smallest perceptible traces of oxygen, hydrogen, carbon dioxide or water vapor completely destroyed it. If the nitrogen were previously passed over heated metallic sodium it did not appear. It seems possible that infinitesimal traces of oxygen may be necessary for its existence, while perceptible traces destroy it.

Recently the writer has discovered additional facts of some interest concerning this afterglow by photographing its spectrum with a quartz spectrograph.

The gas was prepared by heating a solution of sodium nitrite and ammonium sulphate, freed from traces of oxygen by passing through an alkaline solution of pyrogallic acid and dried by passing through a train of drying tubes.

As the phosphorescent glow extended some distance from the electrodes, it was possible to employ a device by which exposures could be made continuously while the discharge passed. A bent tube with a quartz window gave an end-on view of the afterglow, while the direct discharge was screened.

With aluminum electrodes the spectrum was found to be as follows: (1) The four lines in the visible spectrum previously noted, all strong and broad, not as yet identified; (2) the stronger heads of the positive bands of Deslandres' second and third group; (3) the stronger mercury

[1] Lewis, Ann. der Physik, 2, p. 459, 1900; also Astrophys. Jl., 1900.
[2] Warburg, Arch. des Sc. Phys. et. Nat., 12, p. 504, 1884.

lines; (4) four pairs of the strongest ultra-violet aluminum lines; (5) a number of unidentified lines.

On substituting platinum electrodes for the aluminum, the afterglow was unchanged in general appearance, and the visible spectrum and mercury lines remained the same. The aluminum lines were of course absent, while some new lines appeared — apparently not platinum. There were also some strong new bands in the ultra-violet, with heads toward the shorter wave-lengths, which have not yet been identified. The bands of the third group were as strong as when aluminum electrodes were used. Those of the first group were very weak.

The same spectrum was observed with iron electrodes, except that the second group of bands were a little stronger and some lines were absent.

We have in this afterglow apparently a kind of luminosity quite different from any other known in vacuum tubes. The state giving rise to it is due to the previous, not the coexistent discharge, and is far out of its path. The luminosity persists for many seconds after the exciting discharge, and gives not only the band spectrum of the gas, but the line spectrum of metals present in the tube, and other unknown lines.

The body of gas of which the spectrum was observed was at the nearest point about 15 mm. from the direct discharge and extended some four inches from it. Aluminum vapor must have existed in all this region. The phosphorescence followed the first discharge. It cannot, of course, be said with certainty that aluminum vapor took part in the initial phosphorescence — it may have been gradually torn off and diffused. But the remarkable and novel fact is that the aluminum vapor will radiate it all under such conditions. The aluminum lines are relatively the strongest in the spectrum of the afterglow; they are relatively very weak or absent in the spectrum of the direct discharge near the electrodes, where they might be expected to be strongest, if they occur at all.

The sensitiveness of this afterglow to impurities was strikingly shown by an accident. After putting platinum electrodes in the tube, attempts to secure the afterglow failed for several hours. It was finally discovered that there was a very slow leak due to a small crack near one electrode. The leakage was so slow that it made no perceptible difference in the 5-mm. pressure after more than an hour. On covering the crack with shellac the glow appeared immediately after introducing fresh nitrogen.

J. J. Thomson has advanced the hypothesis that afterglow effects are due either to chemical actions in a mixture, or to polymeric changes in a pure gas. If this be the explanation — and it seems a reasonable one — how can a chemically neutral gas excite luminosity in any metallic vapor which may be present, such as mercury and aluminum?

Some light may be thrown on this question by further investigations. Other questions which the writer proposes to attack are: Is the phos-

phorescence possible in absolutely pure nitrogen, or is the presence of any foreign substance necessary? If so, what foreign substance? How active a part do the metallic vapors play? What is the electrical condition of the phosphorescing gas? Do similar afterglows occur in other gases?

Mr. P. E. Rowell rendered efficient assistance in this investigation.